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PROCEEDINGS OF CONFERENCE ON ENVIRONMENTAL ASPECTS OF CHEMICAL USE IN RUBBER PROCESSING OPERATIONS HELD IN AKRON, OHIO, ON MARCH 12-14, 1975

RESEARCH TRIANGLE INSTITUTE

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

JULY 1975

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(MARCH 12-14, 1975, AKRON, OHIO)

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OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
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The objective of this conference was to cover and discuss current chemical use, functions of chemicals in the operations, byproducts likely to be introduced, known health or environmental effects from chemicals used, and measures used or available for use to control environmental contamination. More specifically, papers were presented and discussions held that covered industrial emissions and effluent surveys, chemicals and their effects, reclamation and disposal and academic programs.

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Conference Proceedings

ENVIRONMENTAL ASPECTS OF CHEMICAL USE IN RUBBER PROCESSING OPERATIONS

(March 1975, Akron, Ohio)

Franklin A. Ayer, Compiler

RESEARCH TRIANGLE INSTITUTE
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OFFICE OF TOXIC SUBSTANCES
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FOREWORD

The proceedings for the conference on "Environmental Aspects of Chemical Use in Rubber Processing Operations," is the first of three reports each on a different conference, to be submitted under Contract No. 68-01-2928 to the Office of Toxic Substances for the Environmental Protection Agency. The conference was held at the University of Akron, Akron, Ohio, on 12-14 March 1975.

The objectives of this conference was to cover and discuss current chemical usages, functions of chemicals in the operations, byproducts likely to be introduced, known health or environmental effects from chemicals used, and measures used or available for use to control environmental contamination. More specifically, papers were presented and discussions held that covered industrial emissions and effluent surveys, chemicals and their effects, reclamation and disposal and academic programs.

Dr. Farley Fisher, Chief, Early Warning Branch, Office of Toxic Substances, Environmental Protection Agency, Washington, D.C., was the Project Officer and General Chairman of the conference.

Mr. Franklin A. Ayer, Environmental Technology Department, Center for Technology Applications, Research Triangle Institute, Research Triangle Park, North Carolina, was the Conference Coordinator and Compiler of the proceedings.

Table of Contents

(* indicates speaker)

Page

12 March 1975

Opening Session 1

Welcome and Introductory Remarks 3
Farley Fisher, Ph.D., General Chairman

Keynote Address:
Current Trends in the Control of Chemicals 5
Glenn E. Schweitzer

Session I: INDUSTRIAL EMISSIONS AND EFFLUENT SURVEYS 15
Robert C. Niles, Session Chairman

Odor Sources in Rubber Processes and Their Control 17
Robert E. Kenson, Ph.D.,*
Peter W. Kalika, and
Samuel Cha

Liquid Effluents - Emission Points From Rubber Manufacturing Processes 37
David C. Day, Ph.D.

Secondary Treatment of Wastewater From Synthetic Rubber Production 60
Frederick G. Troppe

Session II: CHEMICALS AND THEIR EFFECTS 87
William E. McCormick, Session Chairman

Toxicology of Acrylonitrile 89
C. Boyd Shaffer, Ph.D.

Alteration Products of Substituted p-Phenylenediamines 99
Henry C. Hollifield, Ph.D.,* and
Pasquale Lombardo

Halogenated Hydrocarbons in Rubber Processing 108
Walter D. Harris, Ph.D.

Panel: CARBON BLACK

Health Studies Relating to Carbon Black 118
Carl A. Nau, M.D.

Carbon Black and Ecology 130
Harry J. Coliyer

Table of Contents (con.)

Page

Carbon Black Adsorbates: A New Carcinogen and Oxygenated Polycyclics 137
Avram Gold, Ph.D.

13 March 1975

Session II: CHEMICALS AND THEIR EFFECTS (con.)
William E. McCormick, Session Chairman

Elastomers in the Health Industries 167
Samuel Koorajian, Ph.D.

The Identification of Effluents From Rubber Vulcanization 185
Stephen M. Rappaport, Ph.D.

Panel: ENVIRONMENTAL DEBRIS FROM TIRES

Airborne Particulate Debris From Rubber Tires 217
William R. Pierson, Ph.D.,* and
Wanda W. Brachaczek

Rubber Dust From the Normal Wear of Tires 274
Mark L. Dannis

Session III: RECLAMATION AND DISPOSAL 313
J. R. Laman, Session Chairman

Panel: RECLAIMING AND RECYCLING RUBBER

Environmental Aspects of Reclaiming and Recycling Rubber .315
Bobby D. LaGrone* and
Edward A. Gallert

Environmental Aspects of Rubber Reclaiming and Recycling (Manufacturing) 349
Robert C. Reinhardt

Panel: TIRES USED AS A FUEL

Shredded Tires as an Auxiliary Fuel 361
Robert H. Taggart, Jr.

The Tire-Fired Boiler 371
William L. Cox
(Delivered by Joe M. Smerglia*)

Scrap Tires and Fishery Resources 331
Richard B. Stone

Table of Contents (con.)

Page

14 March 1975

Session IV: ACADEMIC PROGRAMS 389
Louis S. Beliczky, Session Chairman

Rationale, Scope, and Sponsorship of Academic Programs 391
Louis S. Beliczky

University of North Carolina Occupational Health Studies Program 396
Robert L. Harris, Jr., Ph.D.

The Rubber Workers Study at the Harvard School of Public Health 413
William A. Burgess, *
John M. Peters, and
Richard R. Monson

Session V: CONFERENCE SUMMATION 427
Farley Fisher, Ph.D., General Chairman

Panel: SESSION CHAIRMEN COMMENTS 429

Submitted Papers--Not Presented at Conference 435

Toxicology and Physiological Effects of Phillips Oil Furnace Carbon Blacks 437
Lucian E. Renes

An Economic Evaluation of the Use of Cryogenics in Rubber Tire Reclaiming 442
S. L. Fredericks

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

12 March 1975

Opening Session

Farley Fisher, Ph.D.*
General Chairman

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*Chief, Early Warning Branch, Office of Toxic Substances, Environmental Protection Agency, Washington, D.C.

WELCOME AND INTRODUCTORY REMARKS

Farley Fisher, Ph.D.
General Chairman

Welcome to this conference on environmental aspects of chemical use in rubber processing operations. This is the first conference of this type sponsored by the Office of Toxic Substances, and we hope it is the prototype for conferences on a number of other industrial operations as well.

Our object here is to discuss the use of chemicals in rubber processing--to analyze where these materials may have an effect on the environment, either because of the substances used in the process or because of the types of products produced therein. We are definitely doing this with an attitude of exploration and debate, and we wish for the conference to be lively. In no sense are we trying to restrain people from expressing their views. We have allowed for a large number of question and answer periods, and I hope that you will avail yourselves of the opportunity to ask questions and make comments.

Our keynote speaker for this meeting is Mr. Glenn Schweitzer, who has been Director of the Office of Toxic Substances for about 2 years now. During that period of time, Mr. Schweitzer has been actively involved in the Toxic Substance Program at EPA.

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CURRENT TRENDS IN THE CONTROL OF CHEMICALS

Glenn E. Schweitzer*

The Rapid Growth of Chemical Problems

During the last several years, the number and frequency of harmful incidents involving toxic chemicals have increased dramatically. Hardly a week goes by without a new chemical emerging as an immediate health or environmental problem, and the public outcry over carcinogenesis and other chronic effects of exposure to chemicals seems to have literally exploded.

All levels of government are taking steps in response to the demands for action to clarify and reduce the risks attendant to chemical exposure. No longer are pollution problems viewed simply in terms of esthetics, inconveniences, or ecological degradation; they are now tied more closely than ever before to very personal human health concerns. No longer are the long drawn-out timetables acceptable for corrective steps with regard to toxic chemicals. No longer will the public accept the philosophy that chemicals must be assumed safe until proven hazardous. No longer are latent problems, such as the mutagenic effects of chemicals that may appear only in future generations, to be ignored. No longer are chemicals the unique concern of the manufacturers, the distributors, and their employees, for the Chemical Age of the Seventies has engulfed our entire society.

I need not review for this audience the unsettling chain of events triggered by the linkages established last year between cancer of the liver and exposure to vinyl chloride. Many of the companies represented here have been deeply involved from the outset of this very tragic development, a development rooted in the environmental complacency of the industry during the forties, the fifties, and the sixties. We have all become painfully aware of the difficulties in assessing the risks associated with very low levels of exposure to this chemical and in taking corrective

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*Director, Office of Toxic Substances, Environmental Protection Agency, 401 "M" Street, SW, Washington, D.C. 20460

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actions to reduce these risks. I am sure that all agree that we can and we must do better in the future in preventing these types of tragedies--and particularly in identifying and assessing problems before the fact rather than after the damage is done.

Already tens of thousands of chemicals are in commerce, and the number is increasing every year. Little attention has been given to the environmental properties of many of these chemicals. Constantly evolving research and analytical techniques are revealing that the potential effects of many others are much more extensive than previously suspected. In short, during the years ahead all of us will be exposed to many more chemicals in many more situations, and the list of chemicals known or believed to pose a threat to man or the environment will be greatly expanded.

Our market forces are not designed to insure environmental equity, and the risks and benefits associated with chemicals are not evenly distributed throughout our society. The archaic concept of voluntary exposure to chemicals--that we have a choice as to whether we want to come into contact with chemicals--has been replaced with the hard reality that in fact the individual citizen has little control over the chemicals to which he is exposed. Thus, governmental involvement in the chemical arena will undoubtedly increase to keep pace with the growing chemical burden in the environment.

The Development of the Legislative Basis for Controlling Toxic Chemicals

For many years the Federal Government has been deeply involved in chemical regulation through the activities of the Food & Drug Administration; more recently it has become involved in controlling pesticide use. The Clean Air Act and the Federal Water Pollution Control Act have special provisions directed to toxic and hazardous chemicals in addition to their broader provisions, which also encompass chemical pollutants. Indeed, these activities have to a large extent established the framework for the current spread of programs throughout the industry directed to product safety and environmental control.

During the past several years, the Department of Transportation, the Occupational Safety and Health Administration (OSHA) of the Department of Labor, and the Consumer Product Safety Commission have significantly expanded their efforts directed to toxic chemicals. Of particular interest to EPA and OSHA is the close interrelationship between concerns over chemicals in the workplace and the possible discharges of these same chemicals directly or indirectly into neighborhoods near industrial facilities as the result of air emissions or liquid effluents. In many cases a large share of these nearby residents are the workers who may be exposed to the same chemicals on and off the work premises. Also, we are concerned that in dealing with persistent chemicals, the longstanding approach of better ventilation does not appear to be an acceptable solution to meeting workplace standards.

In December the Safe Drinking Water Act was somewhat unexpectedly enacted. The rapid congressional action on this legislation was prompted by reports of trace amounts of organic chemicals--including several possible carcinogens--found in several drinking water supplies, and particularly in New Orleans. This legislation, which calls for establishment and enforcement of maximum contaminant levels in nationwide drinking water supplies, has far-reaching implications for industry. It seems unlikely that municipalities will invest large sums of money in removing chemical contaminants from their water supplies without first attempting to identify and control the sources of these contaminants. In many cases the sources of concern will undoubtedly be industrial dischargers.

The proposed Toxic Substances Control Act offers an unusual opportunity to improve the soundness and the fairness of regulatory decisions concerning toxic chemicals. The heart of this proposed legislation is the acquisition of more authoritative information concerning both the risks and the benefits associated with chemical activities. Special emphasis is placed on better test information that is predictive of the behavior of chemicals in the environment. A second aspect of this proposed legislation is provision for controlling serious toxic chemical problems that cannot be adequately addressed under other existing authorities.

An improved information base is critical to better decisions concerning Governmental intervention in chemical activities under a variety of regulatory authorities. At the present time, decisions are being made on the basis of very sparse data. Even in the absence of such information, decisions will continue to be made, for action in this field cannot be delayed. In this regard, the lack of hard data concerning chemical behavior should not be considered a license for continued production and use of the chemicals any more than we can assume that activities should cease until they are proven to be absolutely safe.

Intercepting the Problems at the Outset

A main feature of the Toxic Substances Control Act is the emphasis on identifying problems early in the commercial lifetime of chemicals--before there has been irreversible environmental damage and before major economic investments are in place. At present we find ourselves constantly reacting to problem chemicals that are already widely dispersed throughout our economy--chemicals which have already caused environmental problems and which represent substantial investments for suppliers, manufacturers, and distributors. Corrective measures invariably mean substantial economic dislocations.

With 500 to 700 new chemicals being introduced into commerce every year, it is only sensible to make the extra effort to insure that these new products are not going to cause problems later in their lifetime. The extent of the research and testing needed to reach a judgment as to potential environmental problems will vary among chemicals and among uses of the chemicals. However, the ground rules for early assessment of chemicals need sharper clarification and greater acceptance by all concerned. In my view, the recent report of the National Academy of Sciences *Principles for Evaluating Chemicals in the Environment* has been a major step forward in this regard. Further development of the concepts set forth in this report, and particularly relating these concepts to practical problems, needs priority attention.

Of course, any governmental intervention during the premarket phase must be sensitive to the financial realities of R&D activities. Particularly important is the need to avoid additional delays due to uncertainty as to governmental actions. Also, the cumulative effect of actions directed to individual chemicals can dampen the overall climate for research.

Finally, protection of the confidentiality of activities directed to new chemicals is of critical importance.

Unfortunately, this approach of early identification and prevention of environmental problems and economic dislocations will not help in addressing chemicals currently in large-scale production. It is indeed unfortunate that this "pay now and save later" philosophy was not adopted many years ago. As problems continue to arise with high-volume chemicals, the short-term economic adjustments will undoubtedly be severe.

Cost/Risk/Benefit Considerations

Recently the government has significantly increased its efforts to not only assess but also to try to balance the costs, the risks, and the benefits involved in regulating toxic chemicals in the environment. To the extent possible, regulatory activities should be judged on the basis of their total impact on society--impact on the standard of living, effective resource utilization, and preservation of social as well as environmental values.

This change in direction in approaching regulatory decisions has in large measure resulted from a reorientation in the nature of some of the legislative authorities under which EPA operates. For example, the new Safe Drinking Water Act and the proposed Toxic Substances Control Act are very explicit in their requirements to take into account economic as well as health and environmental considerations. On the other hand, certain provisions of the Clean Air Act and Federal Water Pollution Control Act are far from clear as to the weight, if any, to be given to economic considerations. In a related development, recent court action concerning the feasibility of the workplace standard for asbestos has had a considerable impact on the approach of OSHA.

Despite growing sophistication in the approach to controlling toxic substances, rigorous cost/risk/benefit analyses will seldom be possible; for adequate time, data, or resources will usually not be available to satisfy a purist. However, we can certainly do better than we have in the past.

Many of us have had direct experience in attempting to draw conclusions from biological data that are invariably "soft." At the same time, pragmatic economists tell us that their data on benefits may be even softer--and probably characterized by uncertainty, incompleteness, and perishability. They are particularly reluctant to provide estimates of the societal benefits to be derived from the use of chemicals that contribute to improved health and living conditions, to greater personal conveniences, to new recreational and esthetic opportunities, and to maintenance of national defense. Often, they are even less willing to speculate as to how the marketplace will react if a specific chemical is removed or if its price is increased as the result of environmental controls. In short, the economists can provide a shopping list of some of the factors to be considered in regulatory decisionmaking, but they provide relatively little guidance as to how these economic factors are to be weighted or integrated or how they are to be meshed with other considerations.

Several points related to costs seem to be clear, however. If there are increased costs involved in environmental control, these costs will be eventually passed on to the consumer. Secondly, there will probably be local impacts attendant to specific types of regulatory activities, and particularly to limitations on the manufacture or use of chemicals. These local impacts can include business setbacks, employment dislocations, and even depressed real estate values. Finally, the market is in general sufficiently flexible and our innovative capacity sufficently high to fill promptly the vacuum caused by the loss of a single product with alternative products or approaches to providing a similar service.

In view of the critical importance of cost/risk/benefit assessments to responsible decisionmaking, we have recently launched several major efforts to refine the methodologies that can illuminate in advance the implications of regulatory decisions. It is particularly important that value judgments not be disguised in manipulating the data base and that the bases for decisions be structured in such a way that the public can understand the rationale that is used.

The Special Responsibilities of Industry

In recent years, many segments of industry have made very significant investments to control the discharge of effluents and emissions into the environment. These steps have been taken in large measure in response to governmental requirements at the Federal, State, and local levels. There seems to be little doubt that such actions have had a dramatic effect in slowing the rate of degradation of our environment. However, all will agree that we still have a long way to go in cleaning up our air and water and in preserving our landscape.

Similarly, industry has over the years expanded its efforts to insure the safety of its chemical products--safety as viewed from the perspective of the worker, of the housewife, and of the general population. Such efforts have been spurred to a great extent by governmental regulations, in some cases by the latent threat of lawsuits, and at times simply by good business practices. For many years, direct acute effects of chemicals have, of course, been of major concern; and more recently, complementary efforts have been directed to the more long-term and subtle health and ecological effects.

In some cases industry has gone far beyond the requirements laid down by government for pollution control levels to be achieved and for safety requirements. For example, one major chemical company has adopted the near-term goal that all new plants be designed to achieve zero discharge with regard to process liquid waste effluents. Some companies have significantly expanded their staffs of toxicologists to address health problems beyond those of immediate interest in governmental regulations. Other companies are conducting ecological effects tests on chemicals which by regulation are only required to be tested for their health effects. However, our general impression is that most companies are not moving much faster on the environmental front than the rate at which they are required by legally enforceable regulations.

Industry has a special responsibility to know what chemicals are released during its manufacturing activities and during the use of its products. Further, industry has a responsibility to know the levels of human and environmental exposure to chemicals resulting from such releases. Industry has a responsibility to know the likely hazards, if any, associated with such exposures and to insure that the public is aware of these hazards. Finally, industry has the responsibility to take all possible steps to minimize these hazards.

These are societal responsibilities that transcend legal obligations imposed by Federal, State, or local regulations. In the years ahead, these responsibilities must be given equal weight with product performance in judging a company's contribution to society.

To accept these types of responsibilities implies new dimensions in corporate activities, particularly with regard to physical monitoring and to studies of health and environmental effects of chemicals. However, I am optimistic that the industrial leadership of this country will respond to the challenge--that this leadership will show restraint in foregoing attractive commercial activities when necessary in the face of environmental uncertainties, that it will expand its search for less hazardous products, and that it will reward its management for contributions to the health of the Nation and to the conservation of ecological resources with as much enthusiasm as it rewards employees for increasing sales.

A New Departure Towards Common Understanding

This Conference signals a new departure in our efforts to better understand the character, scope, and implications of problems associated with chemical activities. As additional activities in this field are contemplated by government, industry, labor, and other interested groups, it seems imperative that we have an authoritative examination of where we are today--the effect and implications of environmental actions already instituted by government and industry and their future plans and programs. Hopefully, with a common base of understanding, deliberations within government, industry, and labor will be more rational, better balanced, and more objective. In the absence of this common point of departure, there will only be a spiralling of confusion, suspicion, and acrimony on the part of all concerned.

This session, which draws on the expertise and insights of representatives of many of the concerned organizations, is designed to help establish the baseline as to the current situation. Hopefully, the formal program represents but a small portion of the exchanges that will take place during the next 2-1/2 days. We are very encouraged by the large industrial participation in this meeting. Of particular interest to us are the steps being taken by industry. For example, we know that massive R&D efforts are underway to correct the problems associated with PVC activities. To what extent are similar efforts being extended to the rubber processing activities of these same firms that have been so involved with PVC during the past year?

The industry's concern over chloroprene, styrene, and acrylonitrile, for example, have been well publicized. Similarly, government's concerns over gross pollution effects (e.g., BOD, COD, TSS, criteria air pollutants) are being reflected in water effluent permits and in air emission controls. While we should understand these actions, which are important not only in themselves but also as either successful or unsuccessful case histories, probably of even more importance at this Conference is to look ahead into future areas of possible concern--for we all share an overriding interest in substituting preventive for corrective actions.

I am pleased to note that the formal program calls for an examination of progress in pollution control, a review of the characteristics of specific chemicals, a discussion of innovative uses of waste products, and an assessment of the role of epidemiological studies. All of these topics are central to current efforts in controlling toxic chemicals. It seems clear that in the future:

- Pollution control requirements will give much greater emphasis to limiting discharges of selected chemicals;
- The environmental behavior of many more chemicals will be examined in detail;
- Productive uses of waste products will become more and more of a reality; and
- Epidemiological studies to correlate exposure to chemicals with human health effects will expand considerably.

We give high importance to this Conference--which is the first of several such meetings directed to various aspects of chemical usage. This effort is enthusiastically supported by the Administrator of EPA and by the Chairman of the Council on Environmental Quality. We are hopeful that it will make a major contribution to wiser decisions by government and by industry--decisions that can have a significant impact on the price we pay for the fruits of this Chemical Age.

12 March 1975

Session I:

INDUSTRIAL EMISSIONS AND EFFLUENT SURVEYS

Robert C. Niles*
Session Chairman

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*Director of Environmental Control, Oxford Management and Research Center, Uniroyal, Inc., Middlebury, Connecticut.

ODOR SOURCES IN RUBBER PROCESSES AND THEIR CONTROL

Robert E. Kenson, Peter W. Kalika, and Samuel Cha*

Abstract

The processing of rubber employs many chemicals which are potential sources of odor emissions. Solvents, adhesives, antioxidants, and other chemical additives required to manufacture the final rubber products may be odorous in themselves. Additionally, their decomposition products from the rubber processing may be odorous. It is imperative that the difference between potential and actual odor sources in rubber processing be determined. Control technology that abates 90 percent of the air pollution emissions from each process step can be very costly, and yet it may have little or no impact on local community rubber processing odor levels.

Identification and quantification (by dilution to threshold techniques) of odor emission sources in rubber processing and the use of an odor diffusion model can predict which of these sources have significant impact on detectable odors beyond the plant boundaries under the prevailing meteorological conditions. The model, after adjustment so that the predicted and actual community odor surveys are in agreement, can be used to determine the extent of control for each odor source required to make rubber processing odors undetectable in the community.

These techniques can thereby be used to develop a cost-effective odor control system for rubber processing operations. The extent of control required and the nature of the odorous emissions (chemical identity) helps to define the most desirable control technique.

1.0 INTRODUCTION

This paper deals with the subject of odor sources in rubber processing and also describes a basic methodology that can be applied successfully to the definition and solution of odor problems in almost any processing

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*Robert E. Kenson and Samuel Cha, Research Scientists; Peter W. Kalika, Senior Project Engineer; The Research Corporation of New England, Wethersfield, Connecticut 06109.

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industry. The paper will briefly outline the methodology, and as an example of its application, we will discuss the odor problems at a tire manufacturing plant.

The processing of rubber employs many chemicals which are potential sources of odor emissions. Solvents, adhesives, antioxidants, and other chemical additives required to manufacture the final rubber products may be odorous in themselves, and their decomposition products from the rubber processing may be odorous. Control technology which abates 90 percent of the air pollution emissions from each process step can be very costly, and yet it may have little or no impact on community odor levels from rubber processing. Thus, it is imperative that the difference between potential and actual odor sources in rubber processing be determined.

2.0 ODOR IDENTIFICATION

Odor pollution problems do not generally have a counterpart in other forms of pollution whose manifestations are clearly measurable by physical or chemical means. For example, concentration of particulates in the ambient air is measurable directly as a unit of weight per cubic meter of air. Odor pollution involves the response of the human olfactory system to chemical stimuli and the degree of the pollution is related to many subjective factors, including psychological, emotional, and socioeconomic (ref. 1). Thus, if an odorant is detectable in minute concentrations and is offensive, an odor pollution problem certainly exists. On the other hand, large concentrations of certain materials may not be detectable, or if they are, they may have a relatively pleasant odor, and not constitute an odor problem. Therefore, because odors are effects, each odor problem is unique. If plant management attempts to apply a successful solution for one odor problem to what appears to be a similar problem, merely by scaling up or down as required to fit the design to the new source, the intended solution may not solve the problem at all or may cost much more than it should.

While each odor problem is unique, a consistent approach can be used for a solution. The key to effective odor control is always proper definition of the problem.

2.1 Methodology

Most current odor regulations are of the nuisance type which ban the release of objectionable odors but which seldom define how objectionability is to be determined (ref. 2). Therefore, to solve the odor problem, it is usually necessary to achieve essentially zero detectable odor from plant emission sources in the community beyond the plant boundaries. The following steps are designed to achieve this objective:

(a) Conduct an odor survey in the community.

This involves the recognition of odor quality (or characteristic smell) and odor level under different meteorological conditions. This is accomplished by trained observers operating beyond the plant boundaries.

(b) Collect odor samples.

Odor level and standard flow rate measurements are made at each potentially odorous plant emission source. This is done by trained observers within the plant.

(c) Evaluate the effects on community odor levels of specific individual potential odor sources.

This aspect of the program is best done by means of simulation modeling.

These problem definition steps would identify the sources that need to be controlled and what degree of control is needed to eliminate the detectable odors in the community.

3.0 ODOR QUANTIFICATION

An important part of the solution of an odor problem is the quantification of the odor levels. Since odor quantification must always involve the human nose, there are many factors which will affect the results of such quantification. These factors have been grouped into the following two categories:

(a) Sampling - Factors such as sampling container materials, preconditioning of the container surfaces, storage time of the sample, and condensation of moist emissions are the major parameters that have significant effects on the odor sample collection. Details of these effects have been studied by TRC under a Federal Environmental Protection Agency contract and results of this study have been reported (ref. 3).

(b) Dilution-to-threshold measurement techniques--There are many such techniques used, the most widely known (and unfortunately the least reliable) being the ASTM D 1391-57 syringe technique (ref. 4). Recently, TRC was asked by the Division of Air Pollution Control of the State of Illinois Environmental Protection Agency to evaluate the ASTM D 1391-57 technique along with three other dynamic techniques (IITRI olfactometer, Hemeon odor meter, and Misco olfactometer). Other types of devices have recently been reported in the literature (ref. 5).

Whichever dilution technique is used, the measurement involves making successive dilutions of an odorous sample with odor-free air, and presenting the diluted sample to selected odor panelists until the panelists report a detectable odor (ref. 6). The dilutions should be presented in an ascending order, i.e., the most dilute first. Figure 1 shows a diagram of the TRC odor laboratory system. Panel size and panel selection and training are additional parameters which will affect the odor measurement.

3.1 Odor Correlation

Once the potential odor source emissions and the community odor levels have been quantified, they must be correlated. This means that we must assure that the odor levels and types found in the community and those determined for the suspected sources can be related. This is generally done by modeling, either by computer simulation or by wind tunnel modeling techniques. If we cannot relate the sources emissions to the community odors, this could mean that the odor source system is more complex than originally anticipated, or that a significant contribution to the community odor problem has been neglected, or incorrectly represented in the model. For example, building downwash effects could convert a stack emission source into a ground level source.

Figure 2 illustrates the downwash effects and how the most effective stack height was determined by physical modeling (by means of smoke) of a potential odor source.

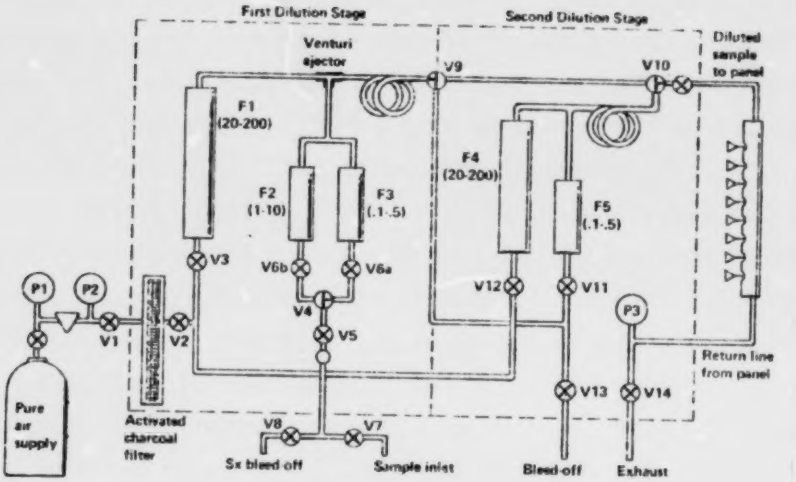

First Dilution Stage
Second Dilution Stage
Venturi ejector
V9
V10
Diluted sample to panel
F1 (20-200)
F2 (1-10)
F3 (.1-.5)
F4 (20-200)
F5 (.1-.5)
V3
V6b
V6a
V12
V11
P1
P2
P3
V1
V2
V4
V5
Return line from panel
V13
V14
Pure air supply
Activated charcoal filter
V8
V7
Sx bleed off
Sample inlet
Bleed-off
Exhaust

Figure 1. Schematic of TRC dynamic dilution odor measurement system.

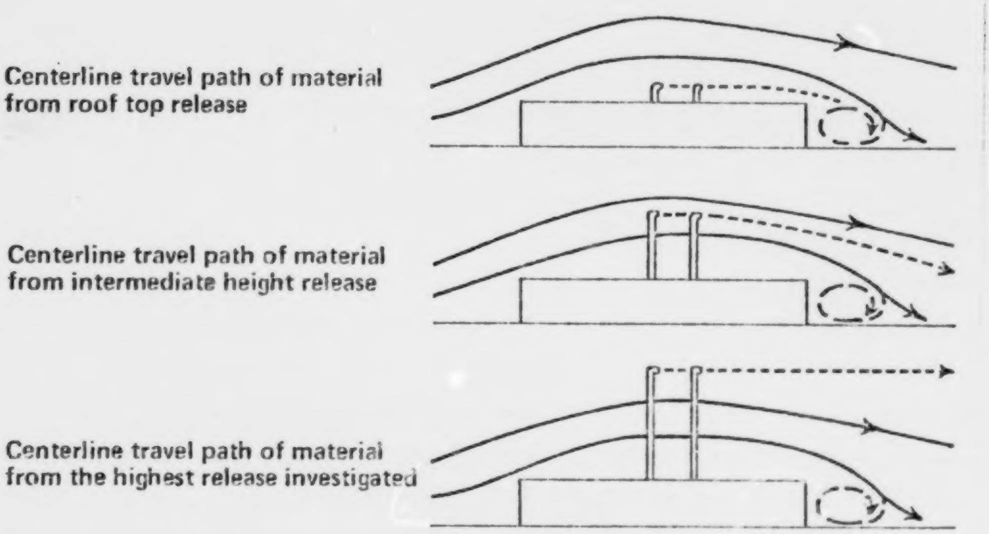

Centerline travel path of material from roof top release
Centerline travel path of material from intermediate height release
Centerline travel path of material from the highest release investigated

Figure 2. Wind tunnel studies with smoke of effective stack height modeling.

Computer simulation modeling involves the application of physical equations describing the diffusion of contaminants in the atmosphere (ref. 7). There are equations available to describe a number of physical situations, including both elevated stack emissions (stacks generally 2 to 2.5 times higher than adjacent buildings) and low level emissions (ground level and elevated line and area configuration sources).

The computer simulations can produce maps of odor concentrations such as those shown for figure 3. These maps show contours of constant odor concentrations (isopleths) in the community that were predicted for different values of stack heights. The example shown is a rubber processing operation. The existing configuration was successfully modelled, then from this result the required stack height to abate the odor problem was determined by adjustment of the stack height parameter input to the computer.

4.0 ODOR CONTROL

When a proper identification of the problem has been made, we are now in a position to determine how this problem can be solved in a cost-effective manner. There is an important decision point here, which requires that we examine the problem carefully to see if either process change or better dispersion of the odorant would be more feasible and cost-effective solutions to the problem when compared to control equipment installation.

4.1 Process Change/Better Dispersion

Process change can often be the most cost-effective method of odor control. Even if complete control of the odor is not possible, this may lead to improved operations (e.g., plugging leaks, closing windows, redesigning hoods) which better confine the odorous emissions and/or reduce total ventilation air volume and thereby lower control costs. As discussed in section 3.1, and shown on figure 3, better dispersion is another potentially viable and cost-effective method. The stack height that meets the criterion of no detectable community odors may, however, not always be in the reasonable cost realm (table 1).

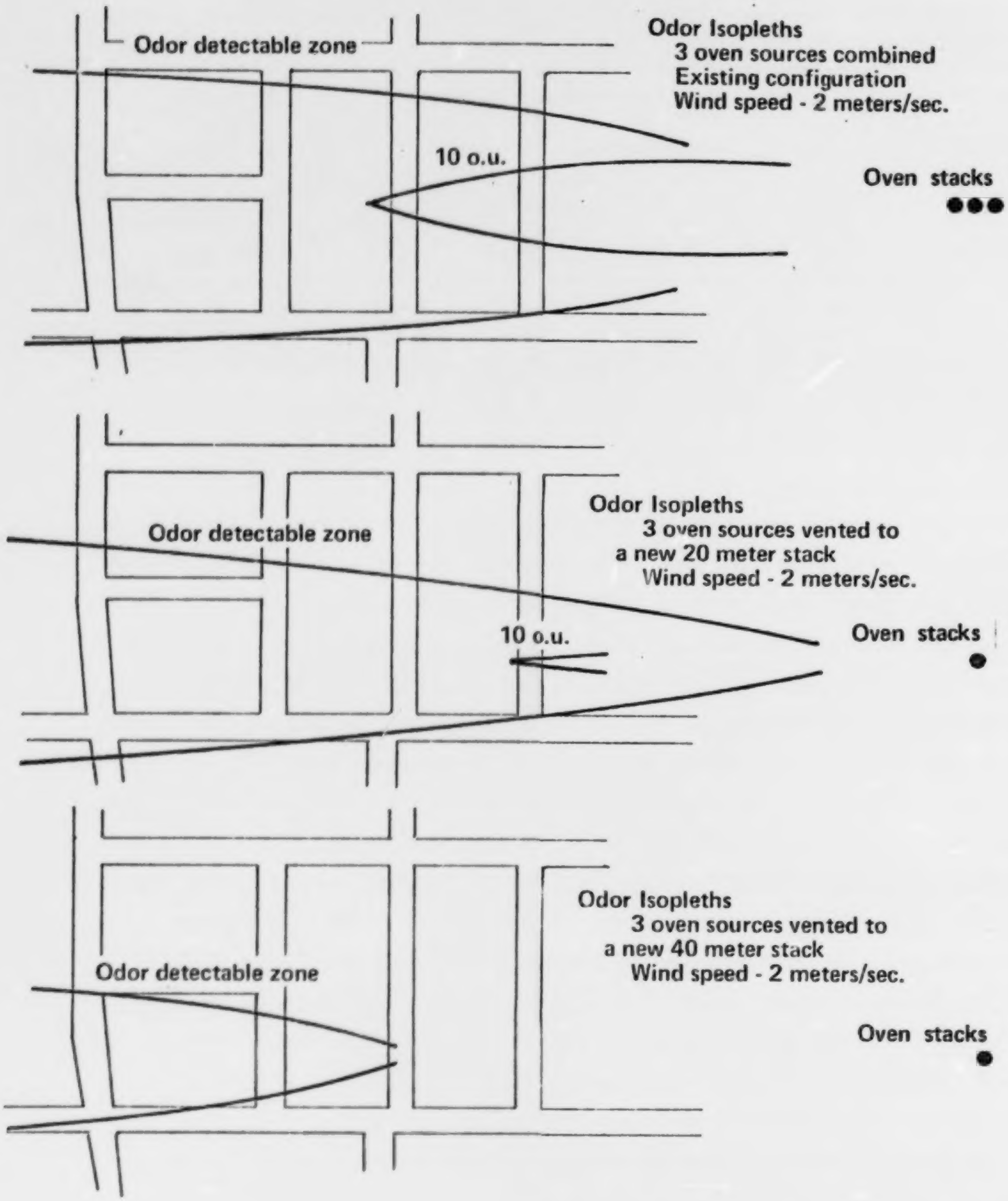

Odor detectable zone
Odor Isopleths
3 oven sources combined
Existing configuration
Wind speed - 2 meters/sec.
10 o.u.
Oven stacks
Odor detectable zone
Odor Isopleths
3 oven sources vented to
a new 20 meter stack
Wind speed - 2 meters/sec.
10 o.u.
Oven stacks
Odor Isopleths
3 oven sources vented to
a new 40 meter stack
Wind speed - 2 meters/sec.
Odor detectable zone
Oven stacks

Figure 3. Odor isopleths for various plant stack heights.

Table 1. Cost estimates for small diameter tall stacks for odor control at one client location*

Height	Construction	Cost (approx.)
50 ft	Guyed-on structure	$ 6,400
100 ft	Guyed-on structure	$ 12,800
200 ft	Self-supported	$250,000
300 ft	Self-supported	$380,000

*These are specific to the case and are meant to show relative costs only. Each odor problem must be treated in the context of the specific emission rates, flow, and meteorological conditions.

4.2 Control Technology

If odor control by other than process change or better dispersion is required, we must first consider the chemical and physical nature of the odorants and other constituents of the gas stream emitted. In many cases, the odorant is a hydrocarbon and the technology of hydrocarbon emission control should be pursued (ref. 8). If the odorant is a water-insoluble hydrocarbon, for example from rubber processing, wet scrubbing may remove particulate matter (e.g., ground rubber) from the gas, but will not control the odor. If instead, we use a carbon bed which is effective for control of the odor, the particulate matter may plug and damage the bed. It is, therefore, apparent that a control technology for one source cannot readily be applied to another source without careful study of the emissions. The uniqueness of each odor problem makes odor control a challenge to the ingenuity of the investigator. Off-the-shelf solutions may be poor and/or costly applications to the problem. Creative design by those experienced in odor control can lead to more cost-effective solutions which will solve the problem without hampering process operations.

The basic control technologies which could be considered for application to solution of odor problems are:

(a) Oxidation
    (1) Chemical
    (2) Thermal
    (3) Catalytic
(b) Condensation
(c) Absorption
(d) Adsorption.

4.2.1 Oxidation

Oxidation is a technique which can solve a wide variety of odor problems. Chemical oxidation, for instance, can be used to remove H_2S odors from rubber-processsing offgases by oxidation to less odorous SO_2 using an aqueous scrubber solution. Permanganate or hypochlorite solutions are among the more effective oxidizing agents. Condensible partially oxygenated hydrocarbons (e.g., some types of paint oven emissions) can be controlled in this manner.

Thermal oxidation is extremely effective in controlling odors from organic-based odorants. Total combustion (>90 percent) of the odorants to CO_2 and water is achieved at about 1200° - 1400°F for most hydrocarbon-based odor sources. It is also an extremely costly solution, especially at current fuel prices, and may be at times the last resort answer for rubber processing hydrocarbon odors if all else fails (refs. 11-13).

Catalytic oxidation promotes the rate of oxidation to allow use of lower operating temperatures and thus saves fuel costs as compared to thermal oxidation. Installed costs are about equal to thermal oxidation, but operating costs should be lower. This method should be considered for hydrocarbon-type emissions such as those found in tire manufacturing. It is important to insure that heavy metals and sulfur-containing compounds are virtually absent from the treated gas stream, since these are virulent catalyst poisons.

4.2.2 Condensation

For concentrated, hot, and odorous vapors that exist as liquids under ambient conditions, condensation may be a feasible technique. Condensers can be readily applied as off-the-shelf control technology, but it must be cautioned that they may transform an air pollution problem into a water pollution problem when contact condensers are used. Condensers may also be considered as preliminary cleanup devices ahead of more sophisticated control systems such as activated carbon adsorbers.

4.2.3 Absorption

Water-soluble odorants can be removed by water scrubbers using this principle. Generally, the scrubbing liquor will contain an oxidant or reactive reagent to convert the odorant to a nonodorous state. Otherwise the odor problem is transferred to the sewer system discharge point or exchanged for a water pollution problem. Organic solvents of low vapor pressure might also be used as a method of concentrating the odorous material, but a recovery or secondary disposal system (e.g., afterburner) will be required.

4.2.4 Adsorption

Organic odorants can be readily adsorbed on porous high internal surface adsorbents such as activated carbon (ref. 14). In the case of high concentrations of hydrocarbons in gas streams, the hydrocarbons can be recovered and recycled into the process. This is a very common odor control method.

There are, of course, problems. If, as previously mentioned, particulate matter is present in the gas stream bed, plugging can occur. Aside from this problem, pressure drop characteristics of the bed can cause certain design limitations (figure 4). The regenerability and cycle time between steam regenerations should be carefully examined before activated carbon is selected for odor control. Figure 5 shows a typical system. Carbon adsorption control systems are a viable technology for application to odorous hydrocarbon emissions from rubber processing, especially for solvents.

5.0 RUBBER PROCESSING ODOR SOURCES AND CONTROL

The odors which can be associated with rubber processing are in many cases detectable beyond the plant boundaries. While the objectionability of such odors can be debated, since this is a subjective response of

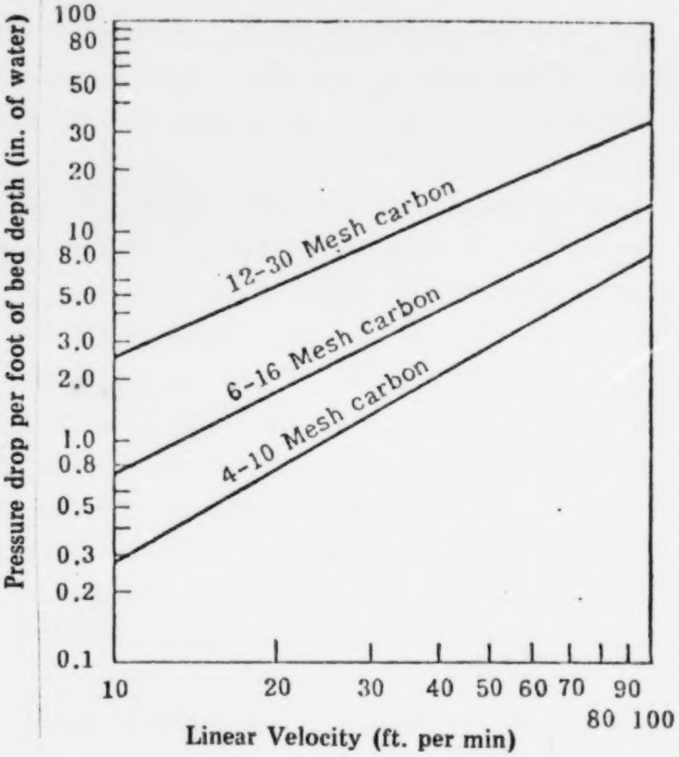
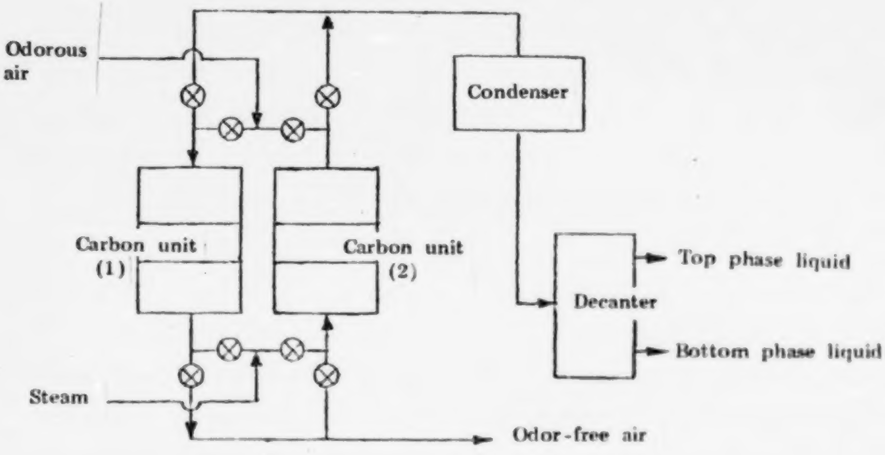


Figure 4. Pressure drop vs flow rate through granular carbon beds.



Odorous air
Condenser
Carbon unit (1)
Carbon unit (2)
Top phase liquid
Decanter
Bottom phase liquid
Steam
Odor-free air

Figure 5. Two-unit fixed bed activated carbon absorber (unit 1 in operation; unit 2 being stripped).

individuals to the odors, the detectability itself indicates a potential community odor problem. In some States, the regulations do not permit any detectable odor; therefore, such odors may already be a nuisance law violation.

If we examine a typical tire plant flowsheet (figure 6), the potential emissions, including odors, occur at several different process locations. They can be emitted through stub stacks, roof monitors, windows, or tall stacks. These potential odor sources in the process, even if they consist of high concentrations of odorous substances and are emitted at a high flow rate, may not produce the odors finally detected in the community. A community odor survey needs to examine the odor levels and the characteristics of the odor detected in order to relate these to the potential odor sources in the tire manufacturing process.

In the tire plant flowsheet, the plastication of the natural rubber after heating and cutting is a potential odor source, since odors from rubber and probably the plasticizer are detectable at the work station involved. In other plants, this operation is sometimes bypassed, and therefore, the Banbury mixer (next operation) is a potential odor source. The odors are basically hydrocarbon (gas and particulate) but also may include gaseous sulfur compounds and oxygenated organic vapors. Another potential odor source is the curing press, where the basic tire is formed and heat-cured with steam. Opening of the press results in release of odorous vapors and gases. This odor is probably a complex mixture of many odorants. They include sulfur compounds (H_2S and organic thiols/sulfides), hydrocarbons (gases and particulates), and oxygenated hydrocarbons (esters, alcohols, aldehydes).

5.1 Other Potential Odor Sources

The other potential sources of odor in the tire-making process are fabric drying ovens (part of the fabric to rubber bonding process) and tire-finishing operations. These odorants probably include vapors of the solvents and cement as well as the rubber itself. Other potential odor sources not so indicated on the flowsheet are any sources where significant quantities of hydrocarbons are emitted or where sulfur-containing compounds are used.

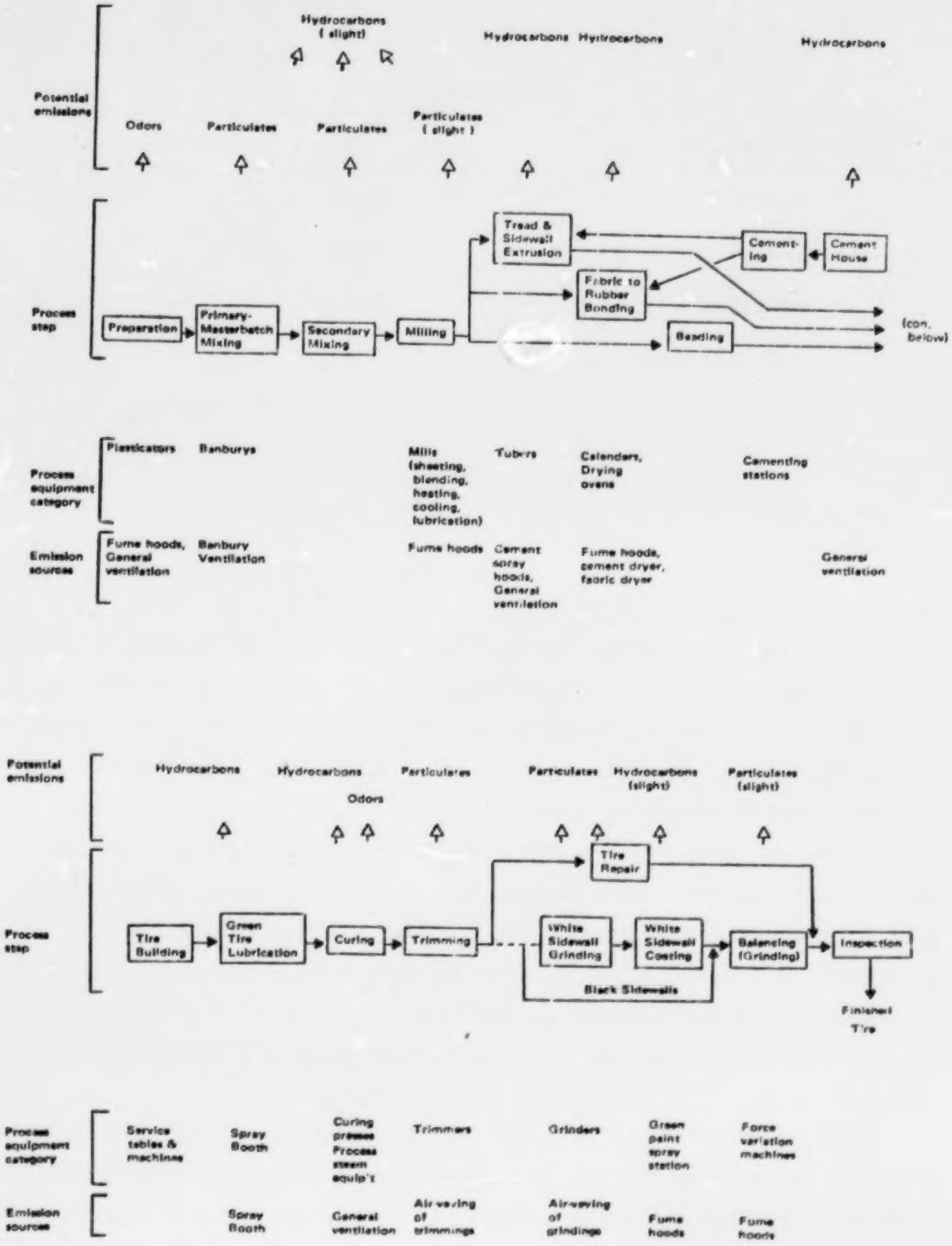

Potential emissions
Hydrocarbons (slight)
Hydrocarbons
Hydrocarbons
Hydrocarbons
Odors
Particulates
Particulates
Particulates (slight)
Process step
Preparation
Primary-Masterbatch Mixing
Secondary Mixing
Milling
Tread & Sidewall Extrusion
Fabric to Rubber Bonding
Beading
Cementing
Cement House
(con. below)
Process equipment category
Plasticators
Banburys
Mills (sheeting, blending, heating, cooling, lubrication)
Tubers
Calenders, Drying ovens
Cementing stations
Emission sources
Fume hoods, General ventilation
Banbury Ventilation
Fume hoods
Cement spray hoods, General ventilation
Fume hoods, cement dryer, fabric dryer
General ventilation
Potential emissions
Hydrocarbons
Hydrocarbons
Odors
Particulates
Particulates
Hydrocarbons (slight)
Particulates (slight)
Process step
Tire Building
Green Tire Lubrication
Curing
Trimming
Tire Repair
White Sidewall Grinding
White Sidewall Coating
Balancing (Grinding)
Inspection
Black Sidewalls
Finished Tire
Process equipment category
Service tables & machines
Spray Booth
Curing presses Process steam equip't
Trimmers
Grinders
Green paint spray station
Force variation machines
Emission sources
Spray Booth
General ventilation
Air vaving of trimmings
Air-vaving of grindings
Fume hoods
Fume hoods

Figure 6. Process flow diagram of a tire manufacturing plant showing odor and other emission sources.

Table 2. Threshold detection values for potential rubber process odorants

Compound	Odor threshold (ppm)*
Styrene	0.05
Xylene	0.08
Toluene	0.17
1-3 Butadiene	0.45
H_2S	0.017 (TRC studies)

*Ref. 6. Concentrations at which 50 percent of the odor panel observed an odor in the working fountain.

5.2 Nonobvious Potential Odor Sources

If we confined our source identification to the inplant detectable odor sources, we still might miss the most significant sources of community odor. Hydrocarbons, that may have a low threshold of detection but are emitted from the tire plant at high rates, may contribute less to the overall community odor levels than more potentially objectionable odorants, which are emitted at low rates (table 2). Another potential source which cannot be ignored is that due to misoperation of air pollution control equipment. One example would be a thermal incinerator operating at too low a temperature or too short a residence time. The result could be the emission of a high level of partially oxygenated odorous hydrocarbon, which may be more odorous than the original uncontrolled emissions.

The evaluation of potential odor sources must be accomplished close to the point of release to the atmosphere, and odor source measurement programs must include all those potential sources whose odor character can be detected in the community or is suspected to be a contributor to the community odor character. Potential odor sources to be measured may include:

(a) Open plant doors and windows;
(b) Roof monitor and local ventilation ducts;
(c) Stub stacks of local hoods;
(d) Main process stacks;
(e) Stacks and vents from air pollution control equipment.

5.3 Odor Source Inventory

If it is complex enough, an inventory of odor sources may be required. Table 3 shows odor emission data from a hypothetical plant that was used to help define the sources of odor in relation to the principal processes carried out in the plant.

It should be emphasized that odor problem identification begins in the community but requires correlation of community odor survey data with potential plant odor sources. A plant odor source not detected in the community is not an odor problem.

Table 3. Odor source inventory for a hypothetical process

Source	Odor level (Odor units/CF)	Source flow rate SCFM	Odor units emissions (Odor units per minute)
Stack #1	400	200,000	80,000,000
Roof vent A	5,000	5,000	25,000,000
Roof vent B	150	5,000	750,000
Roof vent C	350	5,000	1,750,000
Stack #2	1,000	20,000	20,000,000
Stack #3	10	50,000	500,000
Roof monitor	50	80,000	4,000,000
Storage	10,000	200	200,000

Dilutions with pure air required to make source odor undetectable.

Odor level × SCFM source flow rate.

5.4 Rubber Process Odor Control

When considering the control of a given odor problem, the following approaches should be considered in the order listed. In most cases, this would be the order of increasing costs:

(a) Process change;

(b) Better dispersion;

(c) Control technology.

Under control technology, adsorption should be given preference when economical solvent recovery can result from its use. Oxidation (chemical or catalytic) would be the next preferable technology to be considered. Thermal oxidation (incineration) should generally be considered as a last resort, since installation and operating costs, assuming that fuel is available, are high. Under special circumstances, the extensive use of heat recovery techniques such as recuperative heat recovery within the incinerator, makeup air heating, and oven or other process heat, may make incineration a viable alternative.

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DISCUSSION

DR. C. BOYD SHAFFER (American Cyanamid Company, Wayne, N.J.): There was a great deal of information exchanged here about chemicals and the related problems. One of the problems is the odor definition--one of the chemical standbys such as hydrogen sulfide or hydrogen cyanide. My question is, do you think it would be feasible to develop a standard set of descriptions of odors, and if feasible, do you think it would be worthwhile?

DR. KENSON: I think it would be feasible in the long run, but the problem is that you may not be defining the odor problem at all. If it is an industrial odor problem; it is a mixture of odors. A mixture of odors is not always described and defined. There is an interaction of more than one odor. You may have very definite relevance to the choice of sources to apply to a certain chemical, and this is based on the industrial studies. You cannot describe the odors sufficiently to say they are from certain chemicals "x." There may be very much of a mixture.

DR. ABDUL QASI (Union Carbide, South Charleston, W.Va.): First, what odor are we talking about? Secondly, have you done any studies working at changing the stack height? If so, what happened and what is the extent of the odor when you have a wind speed of zero and when the stack height is changed?

DR. KENSON: We are talking about the community odor as detected. This is a very simplistic view, but it is one which can be had by measurement techniques and by models. Zero wind speed is something that is just about never achieved in real situations.

DR. QASI: I mean, under stagnant conditions we have temperature inversion and no movement of air, and the density of warm air increases.

DR. KENSON: This type of problem would cause odors which generally are not odor sources because of the intensified problem effect. In fact, in Los Angeles they found that, during the stagnation period, there were suddenly odor problems and some drastic ones concerning industries, when stagnant air temperature started inversions. In the animal-processing industries, the standards were based upon problems that were not recognized until very stagnant conditions occurred.

DR. QASI: By oxidation of chemicals, is it true that at the same time oxidation would be a worse problem than you have in the given situation? Suppose you have C_2H_5OH. When it oxidizes to a very high extent, it then odorizes more?

DR. KENSON: I agree with you. We have encountered situations, for instance, where an incinerator malfunctioned, causing worse problems. The second implies chemical oxidation. Before we install such equipment, a pilot test should be run, and the odor should be no worse than what we are trying to solve.

DR. QASI: I would like to ask one question. From the studies that you did on the odor emission survey on the tire plant, did you determine that the major principal source of odors came from the application of natural rubber?

DR. KENSON: Basically we find that the first step is to find the primary odor source, but the problem at each plant is to some extent unique. For instance, the ventilation system is different in different plants. This source may be quite different from the one I showed in the hypothetical plant. The source, which is from a tall stack, may be the highest odor-potential emission, may not be an odor source in the community. The one coming out of the roof vent gets downwashed and may be the most severe odor problem. So if I try to generalize

I may get into trouble here, because the specific odor problem is different from the first plant.

MR. KEN CAMINSKY (B. F. Goodrich Chemical Co., Cleveland, Ohio): After listening to the various nuggets from you I am still not sure that an odor problem exists. For example, in the State of Connecticut, they have adopted odor regulations in the State agency. They have one odor, or a concentration of one odor. You can put your subjection in the order of regulations. I think that, even in the City of Cleveland, the indicated odor concentration of 7, 8, 9, and 10 would be acceptable. However, would you give me your opinion, based on current odor technology, as to what a company should have or act on the odor problem? For example, say there is an odor concentration of 50 units, would it be acceptable in order for the company to take any action about that?

DR. KENSON: Basically, you should be in compliance with the law first. Now I presume the public nuisance regulations say that, if someone objects to an odor, there is a problem, which is a violation of the law. The other laws are involved with the various techniques in specifying odors or odor units from the emission source. So the basic statement I first gave is to comply with the law. However, sometimes the law can be subject to the very interpretation given to it. The practical limit of odor detection is odor units in the range of somewhere around 5 to 8, because, when you talk about odor units, you are talking about a trained panelist. But at the same time, there is always going to be somebody possibly objecting to the odor and smell. So my answer is deliberately vague because there is a law to be obeyed.

DR. QASI: Do you believe the time has arrived that we should have a little more sophisticated workman's point of view? The health of the citizen may not be at stake in the criteria, but if we stay below certain levels, you can live with it. We have shown this was not to be adverse to health--something in this regard? What I am saying in this regard is, in other words, that it is possible for a very small amount of odor to cause a few citizens in the community to precipitate a very large expenditure on an odor problem, and I think simply this means a large regulatory criteria.

DR. KENSCN: This is usually the case. It's like anything under the frequency-of-distribution people, as far as why the odor-processing problem is unique. If you try to say yes, a detectable odor is tolerable, instead of saying it is unique and detectable, it becomes so subjective at this time. People are trying to develop this criteria, and they have not.

DR. QASI: One last question--many of the odors associated with the rubber companies in general are due to aerosols. We have found where the classical dilution-type techniques and other chemical tests are not appropriate in determining the odor content of an aerosol. Are there any investigative activities currently under way which will allow us to determine accurately the amount of odor in an aerosol? For example, in engineering techniques and other types of techniques, they simply adhere to the inside of the container in which you accumulate the sample?

DR. KENSON: Basically, you are addressing a problem I am aware of. First of all, an aerosol odor is a rather short-range impact. It is very difficult to model. Secondly, it can only be measured in situ; it cannot be stored--the odors cannot be stored, I agree. Now that odor is actually vapor, the odor carrier, however, can be an aerosol. But basically, the dilution technique must be done at the source; you cannot store a sample, you cannot transfer a sample, and we also have to be careful in our modeling in that we do not overestimate the transport of any odors.

LIQUID EFFLUENTS--EMISSION POINTS FROM RUBBER MANUFACTURING PROCESSES

David C. Day, Ph.D.*

Abstract

During development of the recent effluent limitations guidelines, all significant sources of liquid process effluents from the major segments of the rubber-processing industry were studied. Wastewater characteristics, treatabilities, and applicable control and treatment technologies were evaluated. Based on such factors as these, it was determined that the rubber processing industry could be categorized:

- *Tires and inner tubes;*
- *General molded and fabricated products;*
- *Reclaimed rubber;*
- *Synthetic rubber;*
- *Latex-based fabricated products.*

Process wastewaters from the tire and inner tube industry are principally caused by spills and leaks, and contamination is by tramp machinery oil and miscellaneous solid materials. Accordingly oil and suspended solids are the major wastewater parameters.

Similarly, in the general molded and fabricated product sectors of the industry, most liquor effluents are produced by spills and leaks, and the principal parameters are oil and suspended solids. However wastewater volumes and contaminant loadings differ from those found in the tire and inner tube industry. Potentially, lead is an additional contaminant of the hose industry.

Based on process methods and effluent characteristics, the rubber-reclaiming industry requires further subcategorization: (1) wet digestion reclaiming, and (2) dry reclaiming. The wastewater sources and characteristics from dry reclaiming processes are similar to those from the tire and inner tube industry. However, the wastewaters

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*Project Manager, Southwest Region, Roy F. Weston, Inc., Houston, Texas.

generated by wet digestion plants result primarily from the digestion unit process itself and can be characterized by high COD and BOD loadings in addition to higher levels of oil and suspended solids than found in the tire industry. Furthermore in some older plants, zinc concentrations are significant.

The principal products of the synthetic rubber industry fall into three subcategories: (1) emulsion crumb, (2) solution crumb, and (3) latex. The principal sources of process wastewaters are monomer and solvent recovery operations, crumb coagulation and washing steps, equipment cleanouts, and area washdowns. The significant parameters are COD, BOD, suspended solids, oil, and pH.

Although the latex-based products industry is diverse, one common factor is the use of latex as a raw material and consequently wastewater contamination by latex. Equipment cleanout, product washing, and area washdowns are the major effluent sources, and COD, BOD, suspended solids, oil, and pH are principal parameters. In some cases chromium and zinc levels are significant.

Introduction

Effluent limitations guidelines and new source performance standards have been promulgated by the U.S. Environmental Protection Agency for the major segments of the rubber-processing industry (refs. 1,2). Briefly, the guidelines identify applicable wastewater control and treatment technologies and propose minimum levels of effluent quality for distinct manufacturing categories within the rubber industry:

- Tires and inner tubes;
- General molded and fabricated products;
- Reclaimed rubber;
- Synthetic rubber;
- Latex-based fabricated products.

For reasons of consistency and maximum correspondence with the guidelines, it is convenient to discuss the liquid effluents produced by the rubber-processing industry in terms of the above categories.

The guidelines apply only to process effluents; that is those liquid effluents generated directly by product processes. However, in order to adequately cover the subject of the industry's liquid effluents, it is necessary here to discuss briefly other types of effluent generated by the industry; namely, utility and laboratory wastes.

The intent is to describe rubber industry effluent types and characteristics. Since control and treatment technologies applicable to the industry are diverse and involve many considerations, discussion of the industry's effluent treatment practices is deemed outside the scope of this paper.

Tires and Inner Tubes

The tire and inner tube industry is responsible for the manufacture of a diverse list of products, which includes automobile tires, truck and bus tires, aircraft tires, and "off-the-road" vehicle tires, camelback, and inner tubes. In spite of this fact many of the raw materials, processing operations, and wastewater types are common throughout the industry. Furthermore, most tire and inner tube plants manufacture a mix of products encompassing several of the above product types.

Table 1 presents the waste characteristics of some individual process effluents from typical tire and inner tube plants, and a simplified block flow diagram of a typical tire and camelback production facility is illustrated in figure 1.

Briefly, process effluents from a typical tire and inner tube plant be grouped as follows:

- Spills and leaks of process materials and lubricants;
- Intentional washdowns and cleanup wastes;
- Unintentional cooling water and steam condensate discharges;
- Air pollution control equipment effluents.

The more significant spills and leaks normally arise in storage areas and compounding buildings where oils, compounding materials, and antitack agents are handled and used. In addition, cement and sprays can potentially be spilled in the building and painting areas. If not contained or removed by "dry" methods, such spillages are frequently flushed to the sewer system by washdowns or leaking cooling water.

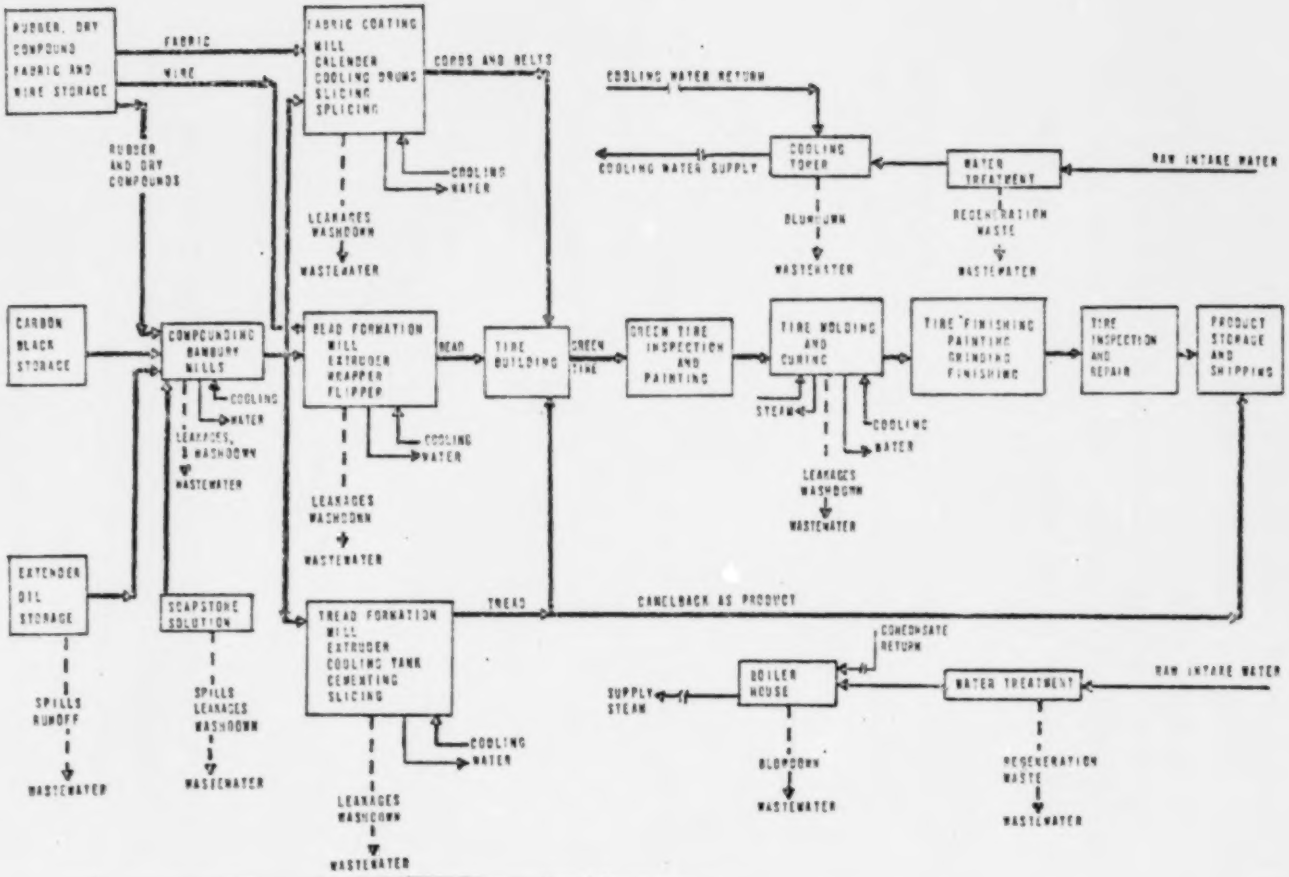

RUBBER, DRY COMPOUND FABRIC AND WIRE STORAGE
FABRIC
WIRE
RUBBER AND DRY COMPOUNDS
FABRIC COATING MILL CALENDER COOLING DRUMS SLICING SPLICING
CORDS AND BELTS
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
COOLING WATER RETURN
COOLING WATER SUPPLY
COOLING TOWER
BLOWDOWN
WASTEWATER
WATER TREATMENT
RAW INTAKE WATER
REGENERATION WASTE
WASTEWATER
CARBON BLACK STORAGE
COMPOUNDING BANBURY MILLS
COOLING WATER
LEAKAGES, & WASHDOWN
WASTEWATER
BEAD FORMATION MILL EXTRUDER WRAPPER FLIPPER
BEAD
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
TIRE BUILDING
GREEN TIRE
GREEN TIRE INSPECTION AND PAINTING
TIRE MOLDING AND CURING
STEAM
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
TIRE FINISHING PAINTING GRINDING FINISHING
TIRE INSPECTION AND REPAIR
PRODUCT STORAGE AND SHIPPING
EXTENDER OIL STORAGE
SPILLS RUNOFF
WASTEWATER
SOAPSTONE SOLUTION
SPILLS LEAKAGES WASHDOWN
WASTEWATER
TREAD FORMATION MILL EXTRUDER COOLING TANK CEMENTING SLICING
TREAD
CAMELBACK AS PRODUCT
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
CONDENSATE RETURN
SUPPLY STEAM
BOILER HOUSE
BLOWDOWN
WASTEWATER
WATER TREATMENT
RAW INTAKE WATER
REGENERATION WASTE
WASTEWATER

Figure 1. Flow diagram of a typical tire and camelback production facility.

Table 1. Typical characteristics of process effluents from tire and inner tube plants

Effluent type	Flow (gpm)	COD (mg/l)	Suspended solids (mg/l)	Oil (mg/l)
Curing press area[a]	31[b]	2,160	546	836
Tread cooling tank overflow[a]	155	40	9	2
Tread cooling tank overflow[c]	155	10	30	-
Wet collector (painting area)[d]	177	188	14	24
Wet collector (sidewall grinding area)[a]	2	860	312	65
Inside drains[e]	0.25	216	15	6

[a] For a plant consuming 18,500 lb/hr of raw materials.

[b] Flow includes water spills and leaks as well as steam condensate leaks.

[c] For a plant consuming 11,000 lb/hr of raw materials.

[d] For a plant consuming 28,000 lb/hr of raw materials.

[e] For a plant consuming 22,000 lb/hr of raw materials.

Although there are few instances in a tire or inner tube plant where water washdown or cleanup operations are necessary, the practice is employed to some degree in most plants. Spilled process oils and solid materials or lubricating oils and greases normally contaminate washdown and cleanup effluents.

Owing to the nature of the industry and the equipment used, cooling water usage by the industry is high. In old plants, once-through cooling water systems are common, whereas newer plants generally employ cooling-tower systems. Although contamination of cooling systems by foreign materials, such as oil, is not a major problem, cooling water leakage in the vicinity of process machinery is relatively common and normally results in flushing contaminants, such as spilled oil or solids, to the sewer system. Condensate leaks at curing presses are common to the industry. In most cases, the leaking condensate picks up tramp hydraulic oil. Although the volume of leaked condensate is relatively low for well-maintained presses, the accumulated leakage nevertheless requires drainage or periodic removal.

In addition to noncontact cooling water used to cool machinery, contact cooling water is used to cool extruded tread and camelback rubber. The flow of such tread cooling water is relatively low and contamination insignificant. In cooling the tread rubber, the temperature of the discharged cooling water is raised approximately 10°F above that of the supply water.

Air emission control devices are normally required for the compounding, spraying, and grinding areas of tire and inner tube plants. Particulates are emitted by the compounding and grinding operations, and three types of control devices, wet scrubbers, bag-house collectors, and cyclones are common to the industry. Bag-houses and cyclones are preferred from a wastewater standpoint but, in some applications, are inappropriate due to binding problems and wet scrubbing devices must be employed. Although it is generally possible to recirculate part of the scrubbing water, some water must be discharged as effluent in order to purge accumulating solids from the system.

The painting or spraying operations of a tire or inner tube plant frequently generate hydrocarbon emissions which are generally difficult or costly to control. Many tire plants are able to use wet scrubbing equipment. Such devices produce an organicsladen effluent. Generally the organic phase is separable and can be removed prior to discharge of the aqueous effluent. Newer technologies, used frequently in other industries, include carbon absorption and thermal or catalytic in cineration and potentially have application in the tire industry. Wastewater effluents from these technologies are normally lower in volume or less troublesome than those produced by wet scrubbing.

In summary, suspended solids and oil are the only significant characteristics of the liquid effluents from tire and inner tube plants. Liquid effluents are produced by spills and leaks, washdowns and cleanups, and air pollution control discharges.

General Molded and Fabricated Products

Rubber products made by molding processes are diverse in size, shape, and end-use. Principal products include hose, footwear, belting, seals and gaskets, and coated fabrics. Processes employed by this industry can typically include compounding, milling, fabrication, molding, and vulcanization.

Although the product mix and number of processes can vary in this industry from plant to plant, most process liquid effluents can be described as:

- Spills and leaks of process and lubricating materials;
- Intentional washdowns and cleanup wastes;
- Unintentional cooling water and steam condensate discharges;
- Air pollution control equipment effluents.

Individual process effluents produced by typical plants in the general molded and fabricated products industry are characterized in table 2.

Spills and leaks from this industry sector are similar in origin and characteristics to those generated by the tire and inner tube industry. Oil and suspended solids are the major constituents. In addition to oil and solid material spillage, latex leaks and spills are a potential problem in both the rubber footwear and coated materials industries where rubber latexes are used as adhesives and coating aids. Latex wastes are usually characterized by suspended solids, COD, and color. The latex spill potential is magnified by the fact that in many cases latex is transported and used throughout the plant in small quantities and by manual methods. Process effluents caused by spillage and leakage should be contained and cleaned by "dry" methods. Latex spills are best coagulated in situ and removed as a solid.

As discussed for tire and inner tube plants, water washdowns and cleanup methods are generally unnecessary, although they are frequently practiced. The most difficult problem created by such practices involves areas where latexes are stored, transported, or used. Ideally all "wet" wash and cleaning methods should be reduced or eliminated completely.

The industry in general has high cooling-water usage supplied by once-through or recirculating systems. In both cases if adequate water segregation or equipment maintenance is not carried out, oil contamination of cooling water or oil pickup by leaking cooling water frequently results. Similarly, leaking steam condensate can be contaminated by tramp oil. The hydraulic oil systems on the compression and transfer molding machines

Table 2. Typical characteristics of process effluents from general molded and fabricated products plants

Effluent type	Product type	Flow (gpm)	COD (mg/l)	Suspended solids (mg/l)	Oil (mg/l)
Spills, leaks,[a] washdown, and runoff	Miscellaneous	7	182	216	-
Spills, leaks,[b] washdown, and runoff	Miscellaneous	16	180	122	-
Spills, leaks,[c] washdown, and runoff	Miscellaneous	52	180	145	-
Vulcanizer[b] condensate	Hose (lead sheath cure)	1	-	63	63
Vulcanizer[b] condensate	Cement-dipped goods and hose (cloth wrap cure)	1	823	10	-

[a] For a plant consuming 5,000 lb/day of raw materials.
[b] For a plant consuming 20,000 lb/day of raw materials.
[c] For a plant consuming 100,000 lb/day of raw materials.

used in the industry lead to a high incidence of oil leaks and spills.

Hose manufacture normally produces a curing-oven condensate which is contaminated by organics or lead, depending on whether a cloth-wrapped or lead-sheathed curing method is used. In either case the condensate volume is low and the contribution of such effluents to the plant's overall effluent is minimal. The organics are leached from the rubber through the cloth wrapping, and presumably small quantities of lead are scoured from the lead sheath by the steam condensate.

Air pollution control devices are used by the industry in the rubber-compounding areas. These can be either wet-scrubber or bag-house type devices. With few exceptions bag-house equipment is successful and scrubber effluents can be avoided. Since product painting and spraying with organic compounds is not practiced in this industry as much as in tire and inner tube plants, "wet" air pollution control devices for this type of service are seldom encountered.

In some plants, such as hose-manufacturing facilities, water is used to hydraulically or pressure test the hose product. In cases where good housekeeping is practiced, little contamination of the test waters occurs. However, if the test water is spilled or poorly drained after use, contamination by tramp solids or oil can occur. Test waters can also be recycled, and the discharge can be eliminated or its volume significantly reduced.

In summary, oil and suspended solids are the principal characteristics for the industry as a whole. Latex solids are an additional constituent in liquid effluents from plants utilizing latex solutions in fabrication processes. Although most suspended solids and oils can be removed by gravity separation, latex effluents require coagulation treatment or ideally should be containerized prior to contract disposal.

Reclaimed Rubber

From a wastewater standpoint, the rubber-reclaiming industry can be subcategorized:

- Pan, mechanical, and dry digester processes;
- Wet digester process.

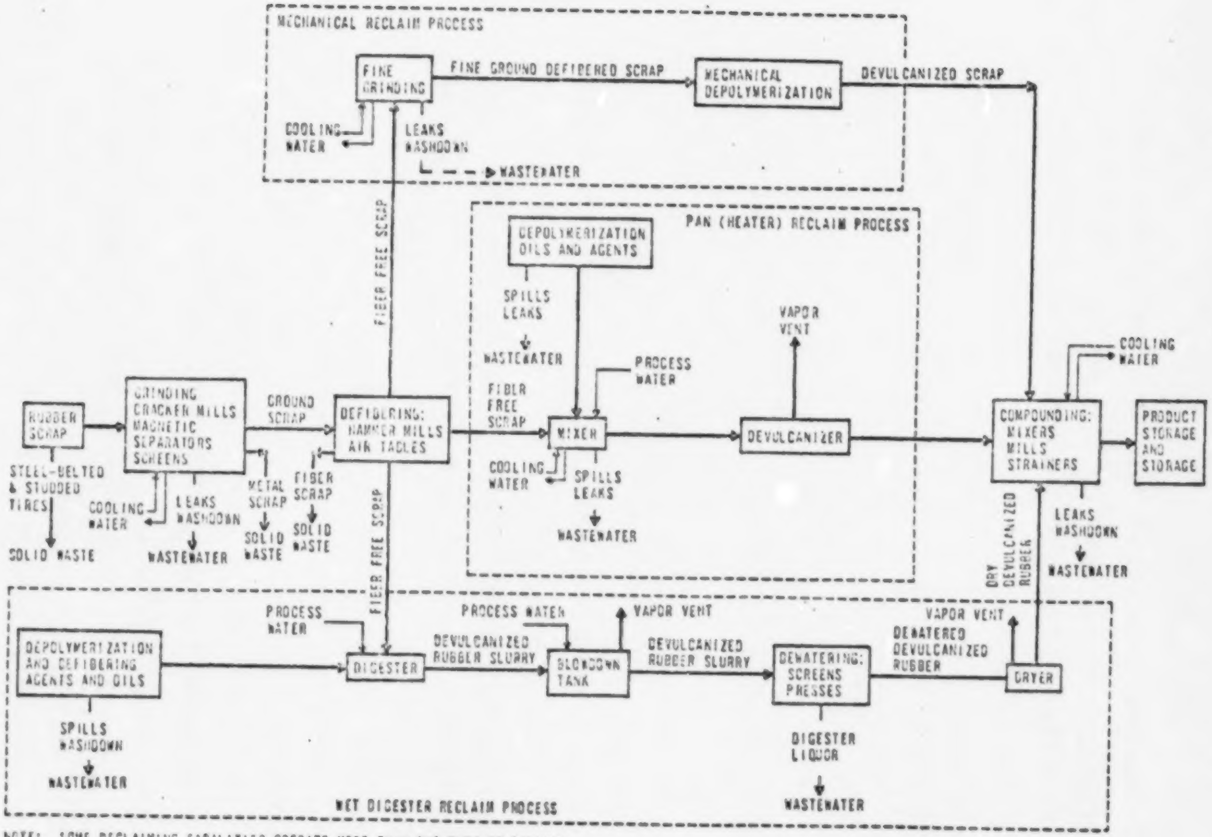
The manufacturing operations occurring at most rubber-reclaiming facilities can be described by:

- Scrap grinding and separation;
- Depolymerization;
- Final processing.

It is in the depolymerization step that the wet digester process differs significantly from the other reclaiming methods.

The wet digester, pan, and mechanical reclaiming processes are presented in simplified block flow diagram form in figure 2. Liquid effluents typically generated by rubber-reclaiming facilities are characterized in table 3.

The operations occurring in the grinding and separation areas are essentially common to all reclaim processes and can be classified as mechanical and "dry" in nature. The principal liquid effluents result from cooling water leaks and water washdowns. The significant characteristics are oil (machinery lubricants) and suspended solids (rubber fines and particles).


MECHANICAL RECLAIM PROCESS
FINE GRINDING
FINE GROUND DEFIBERED SCRAP
MECHANICAL DEPOLYMERIZATION
DEVULCANIZED SCRAP
COOLING WATER
LEAKS WASHDOWN
WASTEWATER
FIBER FREE SCRAP
PAN (HEATER) RECLAIM PROCESS
DEPOLYMERIZATION OILS AND AGENTS
SPILLS LEAKS
WASTEWATER
VAPOR VENT
PROCESS WATER
FIBER FREE SCRAP
MIXER
DEVULCANIZER
COOLING WATER
SPILLS LEAKS
WASTEWATER
RUBBER SCRAP
GRINDING CRACKER MILLS MAGNETIC SEPARATORS SCREENS
GROUND SCRAP
DEFIBERING: HAMMER MILLS AIR TABLES
STEEL-BELTED & STUDDED TIRES
SOLID WASTE
COOLING WATER
LEAKS WASHDOWN
WASTEWATER
METAL SCRAP
SOLID WASTE
FIBER SCRAP
SOLID WASTE
COOLING WATER
COMPOUNDING: MIXERS MILLS STRAINERS
PRODUCT STORAGE AND STORAGE
DRY DEVULCANIZED RUBBER
LEAKS WASHDOWN
WASTEWATER
FIBER FREE SCRAP
PROCESS WATER
PROCESS WATER
VAPOR VENT
VAPOR VENT
DEPOLYMERIZATION AND DEFIBERING AGENTS AND OILS
DIGESTER
DEVULCANIZED RUBBER SLURRY
BLOWDOWN TANK
DEVULCANIZED RUBBER SLURRY
DEWATERING: SCREENS PRESSES
DEWATERED DEVULCANIZED RUBBER
DRYER
SPILLS WASHDOWN
WASTEWATER
DIGESTER LIQUOR
WASTEWATER
WET DIGESTER RECLAIM PROCESS

NOTE: SOME RECLAIMING FACILITIES OPERATE MORE THAN ONE TYPE OF PROCESS.

Figure 2. Flow diagram of typical mechanical, pan (heater), and wet digester reclaim processes.

Table 3. Typical characteristics of process effluent from rubber-reclaiming plants

Effluent type	Flow (gpm)	COD (mg/l)	BOD (mg/l)	Suspended solids (mg/l)	Oil (mg/l)
Pan, mechanical, and dry[a] digester processes					
Spills, leaks, washdown, and runoff	26	110	27	287	154
Vapor condensate from air pollution control devices	2	340	160	8	65
Wet digester process[b]					
Spills, leaks, washdown, and runoff	32	110	27	287	240
Vapor condensate from air pollution control devices	17	240	70	70	480
Dewatering liquor (chemical defibering)	24	3,910	790	106,650[c]	10,770
Dewatering liquor (mechanical defibering)	24	3,910	790	585	10,770

[a] For a plant producing 100,000 lb/day of reclaimed rubber.
[b] For a plant producing 123,000 lb/day of reclaimed rubber.
[c] This value is an estimate and represents a maximum loading assuming all scrap fibers converted to suspended solids.

Depolymerization by the wet digester method is essentially a chemical process and the principal effluent occurs at the dewatering step where the depolymerized rubber solids are separated (dewatered) from the digestion liquor. Since the digestion agents include various oils, organic sulfides, thiols, and amino compounds, the dewatering liquor is characterized by high COD, BOD, suspended solids, and oil.

If the rubber scrap is defibered mechanically prior to digestion, improvements can be made to the digestion and dewatering processes and a significant fraction of the dewatering liquor can be recycled to the digester with makeup of depleted ingredients. Excess liquor is "blown down" from the system, but the net result is reduced levels of COD, BOD, suspended solids, and oil in the effluent.

On the other hand, if the rubber scrap is not defibered mechanically, chemical degradation of the fibrous components must also be accomplished in the digestion step, and this normally requires the addition of caustic soda and calcium chloride to the digester. Accordingly, in such cases the dewatering liquor exhibits alkalinity and extremely large amounts of suspended solids from the fibrous materials and in addition is not suitable for recycle to the digester.

Vapors produced during the digestion process require control. Normally this involves condensing and decantation. With some modification to the digestion process, the decanted organics can be recycled to the digester for reuse, and the need for a wastewater discharge is eliminated.

The pan, mechanical, and dry digester processes are, for the most part, "dry" processes, and most liquid effluents are produced indirectly. Spills, leaks, and washdowns are the major sources and can be characterized by oils and suspended solids. Vapors liberated during the depolymerization process necessitate emission control equipment. Condensation or scrubbing can be used resulting in a liquid effluent characterized by COD, BOD, and oil.

The final stage in all reclaiming processes involves compounding and milling the reclaimed rubber with the required additives. The processing methods are essentially "dry" in nature, and effluents are produced by spills, leaks, and washdowns as well as air control equipment wastes. Spills, leaks, and washdowns are characterized by oil (lubricant) and suspended solids (additives, fines, and soapstone solids) and the effluents from air control devices contain suspended solids produced by scrubbing of particulates and hydrocarbons.

In summary, the effluents produced by the grinding/separation and final processing operations in all reclaiming plants are essentially similar to those produced in tire and inner tube plants and can be characterized by oil and suspended solids. The wet digestion process itself produces a significant liquid effluent containing high levels of COD, BOD, suspended solids, and oil. Chemical defibering, where used, contributes additional suspended solids and some alkalinity.

Synthetic Rubber

Based on the nature of the manufacturing processes, effluent characteristics, and treatabilities, most synthetic rubber production facilities can be subcategorized:

- Crumb rubber;
- Latex rubber.

Owing to several basic processing similarities, it is convenient to discuss jointly the liquid effluents generated by plants producing crumb rubber via emulsion polymerization and solution polymerization processes. The two classes of crumb rubber produce wastewater by analogous operations and, in many cases, in common plant areas:

- Monomer recovery;
- Rubber coagulation;
- Crumb dewatering;
- Equipment cleanout;
- Area washdown.

Monomer recovery and reuse is practiced by the industry in the interests of both process economics and product quality. In most cases this is carried out via steam and vacuum stripping followed by decantation and distillation. Decantation generally produces a monomer-rich layer and a water layer. The water layer is discharged and usually contains dissolved and entrained monomer. Distillation frequently leads to a light monomer cut, a middle water cut, and an organic bottom cut. The bottoms should not be discharged to the sewers since the organic loading is normally very high. It should be incinerated or blended into a compatible organic chemicals feedstock stream. The middle water layer contains moderate loadings of dissolved organics and can be discharged as a wastewater. Solution crumb plants generally combine the solvent and monomer recovery operations. The solvent and monomers are stripped from the rubber product in the stripping-coagulation process. The solvent-monomer-steam overhead stream is decanted and organic layer passes to a distillation unit for separation of the solvent and monomers. The liquid effluents from the distillation and decantation steps are similar to those described above. Monomer and solvent recovery wastes, depending on the nature of the recovery process and on the organics involved, exhibit varying levels of BOD, COD, and oil and grease. The monomer recovery effluents produced by emulsion crumb rubber plants generally contain higher levels of organic loading than those generated at solution crumb facilities.

The coagulation of emulsion crumb rubber is different from that of solution crumb rubber. In the former case, coagulating agents, normally sulfuric acid and brine, are added to the latex rubber producing solid crumb rubber, which is screened from the coagulation liquor. The liquor is returned to the coagulation unit with makeup and a purge stream of the liquor is discharged. This effluent contains acid, brine, dissolved organics, and suspended rubber crumb fines and exhibits low pH, COD, and suspended and dissolved solids. In some cases coagulant mixtures other than acid and brine are used, such as acid-polyamine blends. In such cases, the discharged coagulant liquor contains higher COD and BOD levels and, in addition, has a high nitrogen content.

Solution crumb rubber is generally coagulated during steam stripping. Water and live steam are added to the rubber solution, the monomers and solvent are stripped off, and the coagulated crumb rubber remains. Surfactants are usually added to the stripping-coagulation unit as a means of controlling crumb size. The rubber crumb is screened from the coagulation slurry. The majority of the screened slurry water is returned to the stripper as makeup hot water and the remainder is discharged as a purge stream. The effluent contains dissolved and separable organics, surfactants, and suspended rubber crumb fines and can be characterized by COD, BOD, suspended solids, and surfactants. The strength of the coagulation effluent from solution crumb plants in terms of COD and BOD is considerably lower than the excess coagulation liquor discharged from emulsion crumb facilities. In plants where carbon-extended masterbatch crumb is produced, the coagulation effluent has a significant black color.

After coagulation and the associated screening operation, the rubber crumb requires washing to remove entrained contaminants, such as monomer, coagulation agents, etc. The rinse water is screened and recycled to the wash operation with makeup. A purge stream must be discharged. This effluent contains dissolved organics as well as suspended and dissolved solids and can be characterized by COD, BOD, and suspended solids. In addition, emulsion crumb rubber rinse wastes exhibit some acidity (plus low pH) and solution crumb rinse wastes generated by the two classes of crumb rubber are relatively similar.

Since solution polymerization must be carried out in water-free equipment, virtually no water is used for equipment cleanout purposes. Any equipment cleaning that might be necessary is generally done with solvent. The solvent is then recovered and reprocessed. In emulsion crumb plants, however, considerable quantities of wastewater are generated by equipment cleaning operations and in most cases contamination by latex emulsion results. One major source of cleanout wastes is the stripping columns which must be periodically cleaned of accumulated rubber solids. In most instances cleanout effluents contain dissolved and separable organics and suspended and dissolved solids, and they have a milky coloration caused by the rubber latex content. Cleanout wastes can be characterized by COD, BOD, and suspended solids.

Area washdowns occur in all parts of crumb rubber plants but are more common in emulsion crumb facilities than in solution plants. Common contaminants are organics and rubber crumb solids. Latex spills are frequently washed down in emulsion crumb plants. Washdown effluents contain all the major wastewater characteristics including COD, BOD, oil and grease, and suspended solids. Storm-water pickup from contaminated areas is similar to washdown effluents, although contaminant concentrations generally will be lower.

Three additional sources of effluent contamination that should be mentioned are baler hydraulic oil, extender oil, and carbon black. Leaking hydraulic oil is a common problem in the baling area. Without adequate containment and handling, this oil can reach the plant sewer systems. Extender oil, added to the rubber during the coagulation step, can carry over with the coagulation purge streams and contribute to the effluent oil and grease content. Carbon black storage and handling facilities are generally difficult to keep clean. Storm runoff picks up tramp carbon black, resulting in increased effluent suspended solids and color (black).

In order to prevent premature polymerization during transport and storage, much of the butadiene used by the crumb rubber industry is shipped containing an inhibitor. Prior to processing, the inhibitor is scrubbed from the butadiene using a strong caustic solution. The caustic soda picks up the inhibitor and eventually must be purged from the system as a waste discharge. This effluent has an extremely low average flow rate with high pH, alkalinity, and color (reddish-purple).

Liquid effluents generated in typical emulsion crumb and solution crumb rubber plants are summarized in table 4. Figure 3 is a simplified process flow diagram of an emulsion crumb rubber production facility showing potential sources of liquid effluent.

Table 4. Typical characteristics of process effluents from emulsion crumb and solution crumb rubber plants

Effluent type	Flow (gpm)	COD (mg/l)	BOD (mg/l)	Suspended solids (mg/l)	Oil (mg/l)	Other (mg/l)
Emulsion crumb[a] rubber processes						
Monomer recovery	117	376	62	16	20	-
Coagulation overflow	260	456	-	-	35	16,200(TDS)
Crumb dewatering	1,170	654	44	647	266	-
Caustic inhibitor scrubbing	-	28,000	-	-	-	72,000(alkalinity as $CaCO_3$)
Solution crumb[b] rubber processes						
Solvent monomer recovery	80	-	-	-	8	52(TOC)
Crumb rinse	300	461	-	1,030	447	-
Caustic inhibitor scrubbing	0.25	98,000	-	-	-	-

[a] For plant producing 45,600 lb/hr of emulsion SBR (styrene-butadiene rubber).
[b] For a plant producing 29,000 lb/hr of solution PBR (polybutadiene rubber).

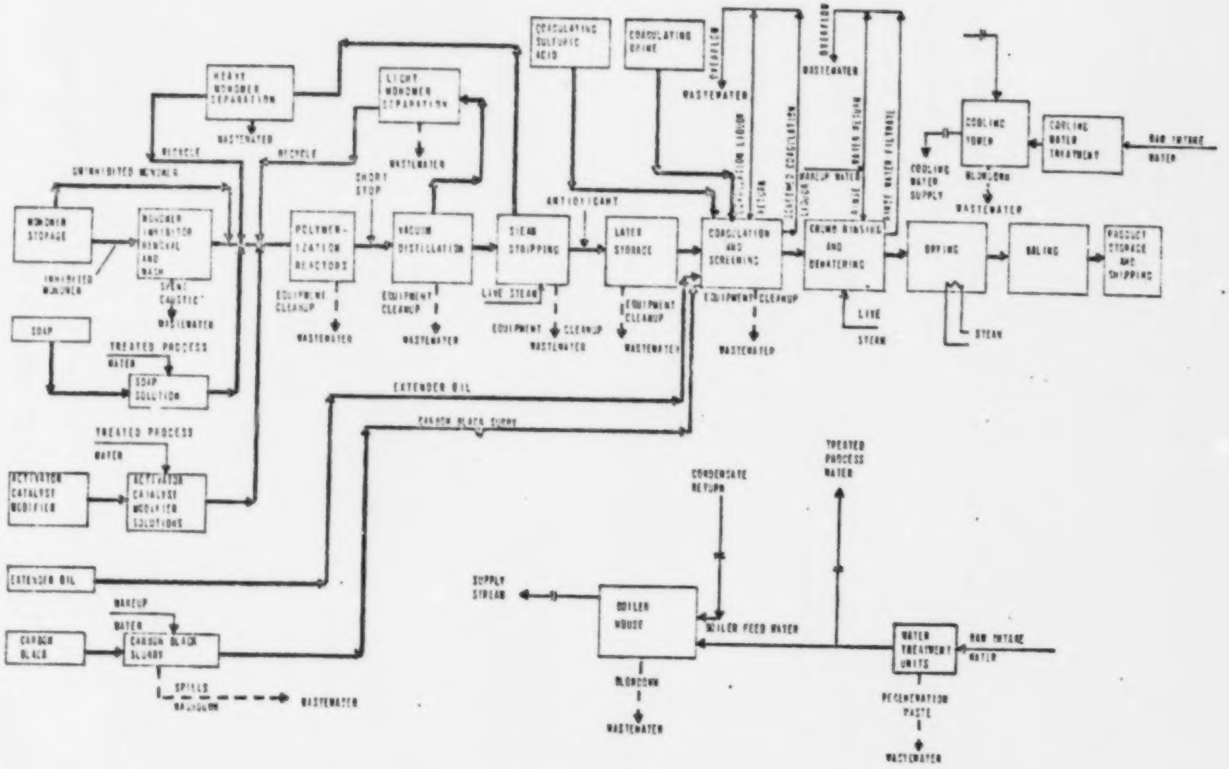

HEAVY MONOMER SEPARATION
WASTEWATER
RECYCLE
RECYCLE
LIGHT MONOMER SEPARATION
WASTEWATER
UNINHIBITED MONOMER
MONOMER STORAGE
INHIBITED MONOMER
MONOMER INHIBITOR REMOVAL AND WASH
SPENT CAUSTIC
WASTEWATER
SOAP
TREATED PROCESS WATER
SOAP SOLUTION
POLYMERIZATION REACTORS
EQUIPMENT CLEANUP
WASTEWATER
SHORT STOP
VACUUM DISTILLATION
EQUIPMENT CLEANUP
WASTEWATER
STEAM STRIPPING
LIVE STEAM
EQUIPMENT CLEANUP
WASTEWATER
COAGULATING SULFURIC ACID
ANTIOXIDANT
LATEX STORAGE
EQUIPMENT CLEANUP
WASTEWATER
COAGULATING BRINE
OVERFLOW
WASTEWATER
COAGULATION LIQUOR
RETURN
SCREENED COAGULATION LIQUOR
COAGULATION AND SCREENING
EQUIPMENT CLEANUP
WASTEWATER
OVERFLOW
WASTEWATER
RINSE WATER RETURN
MAKEUP WATER
RINSE WATER FILTRATE
CRUMB RINSING AND DEWATERING
LIVE STEAM
DRYING
STEAM
BALING
PRODUCT STORAGE AND SHIPPING
COOLING TOWER
COOLING WATER SUPPLY
BLOWDOWN
WASTEWATER
COOLING WATER TREATMENT
RAW INTAKE WATER
EXTENDER OIL
CARBON BLACK SLURRY
TREATED PROCESS WATER
ACTIVATOR CATALYST MODIFIER
ACTIVATOR CATALYST MODIFIER SOLUTIONS
EXTENDER OIL
MAKEUP WATER
CARBON BLACK
CARBON BLACK SLURRY
SPILLS WASHDOWN
WASTEWATER
SUPPLY STEAM
BOILER HOUSE
BLOWDOWN
WASTEWATER
CONDENSATE RETURN
BOILER FEED WATER
TREATED PROCESS WATER
WATER TREATMENT UNITS
RAW INTAKE WATER
REGENERATION WASTE
WASTEWATER

Figure 3. Flow diagram of a typical emulsion polymerized crumb rubber production facility.

Owing to differences in the size of typical plants as well as the form of the final product, the latex rubber industry can best be discussed separately from the crumb rubber industry. Since crumb rubber is not the final product of this industry, crumb coagulation and dewatering effluents are not generated. The principal liquid effluents from latex rubber plants are generated by:

- Monomer removal;
- Equipment cleanout;
- Area washdown.

Because the polymerization reaction is taken almost to completion, recovery of excess monomer is not practiced in latex plants. However, in the interests of product quality, excess monomer is removed from the latex prior to shipment. This is usually done by vacuum stripping, or steam stripping, or a combination of both. Steam jet-barometric condenser systems are commonly used in the stripping operation. The stripped monomer and condensate mixture is either discharged directly or decanted, resulting in an effluent water layer. In either case the effluent contains dissolved and separable organics and can be characterized by COD, BOD, and oil and grease.

Due to shorter production runs and multiproduct-processing operations, more equipment cleaning occurs in latex plants than in crumb rubber facilities. Typically, tankage, reactors, and stripping units are by spray and rinse-out procedures. Similarily, shipment equipment, such as railroad tank cars and road tank trucks, are cleaned frequently, usually by rinsing with large volumes of water. The effluents produced by these cleaning operations contain dissolved organics and suspended and dissolved solids. Latex contamination, with its associated milky color, is invariably present.

Area washdowns are more common in this industry than in crumb rubber plants and occur predominantly in polymerization, blending, and shipping areas. The contaminants are similar to those of cleanout effluents and can be characterized by COD, BOD, and suspended solids.

Latex plants using inhibited butadiene monomer frequently generate the low-volume caustic scrubber waste with characteristics and flow rates comparable to those described above for crumb plants.

Latex-based Fabricated Products

Although the product types manufactured by this industry are diverse, two segments of the industry use the majority of the latex consumed by the whole industry and consequently are the most significant:

- Dipped goods;
- Latex foam.

Process effluents from dipped goods manufacture are generated in the following operations and plant areas:

- Product washing, cooling, and rinsing;
- Form cleaning;
- Tankage cleanout;
- Area washdown.

Prior to curing, the dipped goods, still on the forms, are washed to remove soluble constituents from the rubber. After curing, the rubber items are cooled in a cooling tank and removed from the forms. Frequently a detergent solution is used to facilitate the removal. The items are then rinsed prior to drying, packaging, and final shipment. The effluents from the washing step, cooling tank, and rinsing operations contain dissolved organics and suspended and dissolved solids, and can be characterized by COD, BOD, and low suspended solids.

Periodically it is necessary to clean the forms to remove accumulated rubber deposits. Procelain forms can be cleaned in a chromic acid bath and then rinsed clean. Such rinse waters contain hexavalent chrome which generally requires removal prior to discharge. The other common cleaning method is simple scrubbing with cleaning agents or detergents followed by rinsing. The rinse water usually contain surfactants or suspended solids. In most cases, regardless of the cleaning method, the rinse waters carry suspended and dissolved solids and can be characterized by COD, suspended solids, and surfactants or hexavalent chrome.

Because of short production runs and the general nature of the industry, tank cleaning is common. Normally, simple rinsing techniques are used and the resulting wastewaters contain dissolved organics and suspended and dissolved solids. Rinse waters are usually laden with latex solids and exhibit a milky color. Such effuents can be characterized by COD, BOD, and suspended solids.

Area washdowns are common to the industry and occur most frequently in the storage and dipping areas. The most significant contaminant is latex solids. COD, BOD, and suspended solids are the principal characteristics of the washdown effluent.

The effluents generated by the latex foam industry have higher flow and loadings than those produced by depped goods manufacture. In addition foam product rinse waters generally contain zinc. The zinc originates from the gelling agent mixture which is added to the latex foam prior to the curing step and is instrumental in the curing reaction. The zinc laden rinse water requires zinc removal prior to discharge. Other constituents of the rinse effluent are dissolved organics, and suspended and dissolved solids. The rinse water can be, therefore, characterized by COD, BOD, suspended solids, and zinc.

Liquid effluents potentially discharged by typical dipped goods and foam-manufacturing facilities are summarized in table 5.

Utility Effluents

Like most manufacturing industries, the rubber industry uses cooling water, steam, and treated water. The effluents produced by such service facilities, termed here utility effluents, include;

- Water treatment wastes;
- Boiler blowdowns;
- Steam condensate;
- Cooling-tower blowdown;
- Once-through cooling water.

Since the above effluents are not unique to the rubber industry, it is not necessary to describe them at length. Table 6 is a brief description of the characteristics commonly found in utility effluents.

Once-through cooling waters are discharged directly and contribute high flows together with residual quantities of treatment chemicals. Cooling tower blowdowns, on the other hand, have lower flows and potentially contain higher levels of treatment chemicals. Additional contaminant loadings can be present in both once-through cooling water

Table 5. Typical characteristics of process effluents from latex-dipped goods and latex foam plants

Effluent type	Flow (gpm)	COD (mg/l)	BOD (mg/l)	Suspended solids (mg/l)	Surfactants (mg/l)	Zinc (mg/l)
Latex-dipping processes						
Spills, leaks, washdown, and runoff from latex-handling areas	-	-	-	3,900	-	-
Product wash and rinse water (single wash)[a]	34	176	133	78	2	-
Product wash and rinse water (multiple wash)[b]	63	108	24	9	2	-
Latex foam-manufacturing processes						
Foam rinse waters[c]	60	13,230	4,900	7,000	25	975
Spills, leaks, washdowns, and runoff from latex-handling areas[c]	10	29,180	3,620	1,200	3	33

[a] For a plant consuming 9,500 lb/day of latex solids.
[b] For a plant consuming 2,000 lb/day of latex solids.
[c] For a plant consuming 200,000 lb/day of latex solids.

and cooling-tower-system discharges if process or lubricating materials are allowed to enter the systems.

Boiler blowdowns are generally low-flow effluents, characterized by dissolved solids and high temperature and sometimes alkalinity. Associated with steam-generating operations are the boiler feed water-treatment facilities. Depending on the characteristics of the supply water and the type of boiler equipment, water treatment effluents can include clarification solids, softening regenerants, and deionization backwashes.

In addition, the synthetic rubber industry and latex-consuming industries consume treated water in preparation of latex rubber emulsions and blends.

Table 6. Summary of utility effluents

Source	Effluent Type	Common characteristics
Water treatment wastes		
Clarification	Clarifier and filler solids	Suspended solids, coagulation aids, pH
Lime softening	Clarifier solids	Suspended solids, high pH
Zeolite softening	Brine regeneration-tion	Dissolved solids
Deionization	Acid/Alkali regeneration	Acidity, alkalinity, pH
Boiler blowdown	Blowdown	Dissolve solids, temperature
Steam condensate	Waste or nonreturned condensate	Process contaminants, temperature
Cooling-tower blowdown	Blowdown	Suspended and dissolved solids, chromium, zinc, COD, process contaminants
Cooling water	Once-through water	Process contaminants

Laboratory Effluents

Most manufacturing facilities in the rubber industry have laboratory operations for product quality control and raw material assay purposes. The liquid effluents generated by such facilities generally have low volumes but potentially can contain corrosive, toxic, or explosive constituents. In some instances where process effluents are not appreciable in both flow and concentration, laboratory wastes can contribute a significant proportion of the total organic loading from the plant.

REFERENCES

1. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Tire and Synthetic Segment of the Rubber Processing Point Source Category," Government Printing Office, Washington, D.C.

2. U.S. Environmental Protection Agency, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Fabricated and Reclaimed Rubber Segments of the Rubber Processing Point Source Category," Government Printing Office, Washington, D.C.

DISCUSSION

OBSERVER: Can you tell us if, from your experience, you have any opinion of any specific organic chemicals in tires that would be toxic in the water?

DR. DAY: My experience with the rubber industry has involved study of gross pollution parameters only, such as BOD, oil, grease, and suspended solids, and not toxic materials in detail. Therefore, I feel I am not qualified to discuss the toxic nature of some of the compounds experienced in the rubber industry. This is a separate type of study that would be required. I am sorry I cannot help you.

MR. ROBERT C. NILES (Uniroyal, Inc., Middlebury, Conn.): I would like to add a postscript to Dr. Day's presentation. Many of you may be aware that Public Law 92.500, Section 515, established the Effluent Standards and Water Quality Information and Advisory Committee, of which Dr. Martha Sager is chairman. This committee recommended to EPA very early in the phase of developing effluent guidelines in industry that the matrix model system should be considered. The Rubber Manufacturers Association contracted with the Industrial Water Quality Management, the Center for Industrial Water Quality of Vanderbilt University, to develop the matrix model for tire plants. This study has just been completed this week, and if any of you are interested and would like a copy, you may contact Mr. Frank Ryan of the RMA office in Washington to secure a copy. The significant aspect of the study indicated that perhaps the industry should be divided into two categories, those plants built after 1945 and those built prior to 1945. It was also indicated that there was a substantial difference between the 30 days' average and the daily maximum value of the perimeter study. If any one is interested, Dr. James H. Clark from Vanderbilt is here, and I am sure he will be pleased to discuss with you the ramifications of this study.

SECONDARY TREATMENT OF WASTEWATER FROM SYNTHETIC RUBBER PRODUCTION

Frederick G. Troppe*

Abstract

Secondary treatment of wastes generated from synthetic rubber production was studied for a 9-month period. Its design criteria were flow of 3.55 MGPD and effluent reductions of BOD_5 *by 90 percent and suspended solids by 95 percent to 7 mg/l and 10 mg/l respectively. Average reductions of 84.2 percent for* BOD_5 *and 85.2 percent for suspended solids were achieved.*

The treatment processes included neutralization, coagulation, flocculation, primary clarification, biological treatment, final clarification, and sludge impoundment. Dissolved air floatation aids clarification, while aeration provides biological treatment. Raw wastewater was characterized by the presence of salt brine, dilute acid wastes, boiler blowdown, dilute latex, and coagulated rubber solids. Influent concentrations were: BOD_5*, 72 mg/l; COD, 447 mg/l; suspended solids, 197 mg/l.*

Of the total project cost in excess of $2,000,000, approximately 25 percent was utilized to segregate process wastewater from storm water. The average costs for operation, maintenance, and depreciation were $0.50 per 1,000 gallons of wastewater treated.

INTRODUCTION

Each and every time an industrial process uses any portion of its environment, whether it be air, water, or land, that process inherently generates a waste load that must be returned to a respective disposal site. Ideally, this waste load is returned to the environment with minimal effects, at least within the assimilative capacity of its disposal site.

The manufacture of synthetic rubber offers no exception to this use-disposal scheme. It is estimated from our studies that for each long ton of rubber produced, 4,500 gallons of water-use are required. Since daily production at the Firestone Plant in Lake Charles, Louisiana, is about 800 long tons, the magnitude of its effluent treatment needs is immediately felt. Of the 3.55 million gallons per day of wastewater, approximately 85 percent is generated by the emulsion polymerization process. Wastewater incident to solution polymerization is significantly less because polymerization occurs in a solvent medium instead of in a water emulsion, thus eliminating the coagulation step in the process. A majority of the water usage is indirect such as in power utility and noncontact cooling.

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*Project Engineer--Environmental, The Firestone Tire and Rubber Company, Akron, Ohio.

In light of anticipated effluent guidelines, this development study to treat the plant's effluent was undertaken because it represented a recognized, potential effluent problem. Since no previously tried or proven technology for the treatment of wastewater from the synthetic rubber production had existed, partial sponsorship was received from the Federal Environmental Protection Agency under demonstration grant no. 12110GLP. Its objective was to demonstrate the feasibility of treating a synthetic rubber wastewater using the various staged techniques of neutralization, chemical coagulation and flocculation, primary and secondary clarification, and biological treatment. The economics and efficiency of this treatment system would be reflected in:

a) The utility of dissolved air flotation clarification for suspended solids removal;

b) The successful removal of 90 percent BOD_5 and 95 percent suspended solids;

c) The BOD_5 and COD removals via completely mixed aerated lagoon with 1-day retention;

d) The capital, operating, and maintenance costs incurred.

Similar production facilities and manufacturing techniques would produce similar wastes. However, dissimilar disposal sites would dictate radically different effluent limitations. In order to find a flexible, long-range solution to the problem, only an expandable, parameter-withdrawal technology was considered to be a logical approach.

BACKGROUND AND THEORETICAL CONSIDERATIONS

Since the treatment of synthetic rubber wastewater requires numerous separation techniques and physicochemical processes, it follows accordingly that the fundamentals of colloids, chemical coagulation, flotation, and bio-oxidation via aeration must be applied.

Colloids

Most materials in a suspended or colloidal form cannot be removed by mere settling. Exhibiting large surface area-to-volume ratios, colloids cannot be separated by conventional physical treatment methods. However, surface phenomena, e.g., adsorption, electrostatics, provide the rate-controlling mechanisms for particle growth and removal.

Colloids can be hydrophilic, surrounded by a water layer hindering contact and aggregation with other colloidal particles, or they can be hydrophobic, maintaining stability by the mutual repulsion of similarly charged colloids. In both cases, an overall condition of electroneutrality must be satisfied. A hydrophilic particle derives its charge by ionization, being dependent on the pH of the medium; whereas the hydrophobic particle is charged by localizing excess electrical charges and attracting counter-ions to create an electrical double layer.

The electrostatic potential at the shear surface of the double layer is called the zeta potential; its magnitude directly affects the stability of the colloid. The dispersion of a colloid remains stable as long as the zeta potential exceeds the value from contributions of gravitational and van der Waals forces. Once this condition is reversed, the colloid is destabilized and aggregation can occur. If solvation of hydrophilic colloid is weak, destabilization is accomplished by neutralization and adjustment of the pH to the isoelectric point where no net charge or double layer exists.

According to the Schulze-Hardy rule, the ion used to destabilize a colloid is most effective if it is trivalent and to a lesser degree a bivalent ion. Coagulants of a trivalent nature, i.e., iron III and aluminum III, can effect chemical coagulation successfully if a proper pH allows a sufficiently high concentration of metal ions to precipitate hydroxides. The hydroxide floc formed sweeps the dispersion together and entraps particles in the floc.

Various polyelectrolytes, activated silica, and bentonite promote and enhance coagulation by chemically bridging the occluded particles with the floc.

Flotation

Once the particles have been conditioned for destabilization and aggregation begins, the floc solids have three response choices possible within the medium: settling by gravity, remaining in suspension, or floating to the surface. Since all three will be present to some degree, it is logical to force all solids to the surface by flotation. There are three basic types of dissolved air flotation systems: 1) pressurization of the total influent liquid, 2) pressurization of part of the influent stream, and 3) recirculation and pressurization of a clarified effluent fraction.

In this last case, a portion of the clarified effluent is pressurized, e.g., 40-65 psig, with sufficient air to approach saturation. When this portion is combined with the bulk liquid, micron-sized air bubbles are released because the solubility of air in water varies directly with pressure, solubility being inversely proportional to temperature. The air bubbles become occluded within the floc particles or adhere to the suspended solids, buoying them to the surface.

Solid-liquid separation by flotation is governed by Stokes' Law:

$$v = \frac{{}_{g}D^{2}(d_{s}-d_{l})}{18\mu} \qquad (1)$$

The density difference of the air-solid particle versus the liquid medium provides the driving force. Because of convention, the velocity is negative if the particle is floated.

For a given temperature, the theoretical quantity of air released when pressurized and then reduced to atmospheric pressure may be calculated from:

$$s = s_a \frac{(f\ Pa)}{14.7} - 1 \qquad (2)$$

where s = amount of air released, cm^3/l

s_a = air saturation at atmospheric pressure, cm^3/l

P_a = absolute pressure, $lb/in.^2$

f = fraction of saturation attained.

The actual amount of air released depends upon the turbulent mixing conditions and design of the pressurization system. This, in turn, will reflect the performance of a flotation unit by relating the mass of air released per unit mass of solids in the influent liquid. An air/solids ratio can be calculated directly by the following equation (ref. 1):

$$\frac{A}{S} = \frac{Cs_aR(f\,P-1)}{QS_a} \qquad (3)$$

where C = air density, mg/cm^3
R = pressurized volume, liters/day
P = absolute pressure, atm
Q = waste flowrate, liters/day
S_a = influent suspended solids, mg/l

There naturally will exist a practical limit for an air/solid ratio, above which turbulence destroys floc formation and decreases removal efficiency.

Biological Oxidation

Biological wastewater treatments are natural, spontaneous, self-purifying processes that will proceed under specific and controlled conditions. There are two basic processes that remove organic matter from wastewater via oxidation and cell synthesis.

$$\text{Organic matter} + O_2 + NH_3 \xrightarrow{\text{(cells)}} \text{New Cells} + CO_2 + H_2O \qquad (4)$$

$$\text{Cells} + O_2 \longrightarrow CO_2 + H_2O + NH_3 \qquad (5)$$

Under aerobic conditions, microorganisms use dissolved oxygen as a respirable food to fuel its conversion of organic wastes into cellular matter. If there exists a low food-to-microorganism ratio, endogenous metabolism occurs. As a result the amount of cellular matter consumed is also affected by the average sludge age and waste characteristics such as toxicity.

Almost all mathematical models proposed show that at high BOD_5 levels the rate of BOD_5 removal per unit of active biological sludge remains constant to a limiting concentration. Below this level, the rate becomes concentration-dependent and will decrease. The overall removal rate will follow first- or second-order kinetics, depending on the substrate mixture.

$$\frac{a}{X_a}\frac{dL}{dt} = kL \qquad (6)$$

and

$$\frac{a}{X_a}\frac{dL}{dt} = kL^2 \qquad (7)$$

where: a = volatile suspended solids synthesized per unit of BOD_5 removed, mg VVS_p/mg BOD_r

k = substrate removal rate coefficient (or sludge growth rate), 1/mg per hour

L_e = Effluent BOD_5, mg/l

L_o = Influent BOD_5, mg/l

t = aeration time, hours

X_a = concentration of biological volatile solids, mg/l.

Integrating (6), it becomes

$$\frac{L_e}{L_o} = \exp\ (-k\ X_a\ t) \qquad (8)$$

and (7) becomes

$$kL = \frac{L_o - L_e}{X_a t} \qquad (9)$$

or rearranging and solving for "k,"

$$k = \frac{L_o - L_e}{L_e X_a t}\ . \qquad (10)$$

The data from most completely mixed systems in which the effluent BOD_5 concentration is low can be correlated according to equation (9). The removal rate coefficient is temperature dependent, as shown by equation (11) (ref. 1).

$$k_T = k_{20°C} \cdot \Theta \exp\ (T-20) \qquad (11)$$

where: Θ = experimental temperature coefficient

T = temperature °C.

The sludge yield from a biological treatment system can be estimated from the following relationship (ref. 1).

$$X_v = S_o = aL_r - bX_v \qquad (12)$$

where: X_v = sludge yield, mg/l
X_v = average MLVSS in system, mg/l/day
$\underline{a}$ = cell yield coefficient, mg SS/mg $BOD_{\underline{rl}}$
L_r = BOD_5 removed, mg/l
S_o = influent VSS, mg/l.

Sludge yield from biological oxidation may vary for several reasons. The "k" rate in the BOD_5 test may vary, depending on the characteristics of the waste and the microorganisms. Also, variations in the volatile suspended-solids content of the influent wastewater will influence the sludge yield. Probably most important to most industrial wastes is that the rates and concentrations of the influent streams may change markedly during the course of the measurement period.

In practice, biooxidation would be accomplished in an aerated lagoon, which is a waste stabilization pond, typically 6 to 18 feet in depth, outfitted with mechanical surface aerators to provide oxygen transfer through the air-liquid interface. Oxygen is needed for biooxidation as reflected in BOD removal. It has the advantage of not being very sensitive to wide system variations and, therefore, does not require extremely close control of temperature, pH, and organic loading.

Its full potential might be realized if sufficient aeration equipment could be installed to keep the system completely mixed so as to satisfy the necessary O_2 requirements. Often, a turbulence level is maintained only to ensure oxygen throughout the basin. Most inert solids and nonoxidized biosolids will settle to the bottom and undergo an aerobic decomposition. If the turbulence level is sufficient to maintain solids in suspension, the system becomes analogous to an activated sludge process.

Since the level of active biosolids is low in an aerated lagoon, BOD_5 removal becomes primarily a function of retention time, temperature, and the nature of the waste. At equilibrium a small fraction of BOD will remain because autooxidation will continue to release back into solution some minimum level of cellular breakdown products.

PROCESS DEVELOPMENT

Long before the choice of a treatment system can be made, a sound and detailed definition of the problem must be made. This will pinpoint any meaningful design criteria. The intent is to develop an expandable technology permitting parameter withdrawal in step-wise fashion. This method should allow a greater degree of contaminant removal based on the existing quality of the receiving body of water; the quality of effluent being discharged to a sanitary sewer system need not be treated as extensively as that being discharged to a surface stream. In the case of wastewater treatment, flow and waste characterization present but two fundamental questions of how big and to what extent treatment must be.

Each of the following steps was specifically taken by the plant to uncover any extraordinary requirements, and corresponding conclusions were drawn.

(1) A weir was constructed for flow measurement; because of wide fluctuations due to storm runoff, it was prudent to separate process wastes from storm water.

(2) Composite sampling and analysis of the plant's raw wastewater was conducted; the wastewater parameters that are consistent with synthetic rubber production are suspended solids, biochemical oxygen demand, chemical oxygen demand, and oil and grease.

(3) Jar tests were conducted to survey possible chemical treatment; anionic polyelectrolytes of medium charge and high molecular weight are the most effective flocculents at the 0.25-1.0 mg/l level and alum, the primary coagulant, at a 30-150 mg/l level.

(4) Bench-scale air flotation tests (figure 1) were run as a primary solids removal technique; pretreatment with coagulants and flocculents is required. A maximum recycle pressure of 50 psig for air-bubble formation gave good clarification. Higher pressures showed no improvement, while lower pressures produced too large bubbles. A BOD_5 removal of 28 percent suggested that the BOD was dissolved, thus requiring bio-oxidation.

(5) Air flotation was run as a secondary solids removal technique conjunction with bio-oxidation (figure 2); again it is noted that a flocculent aid is required for effective clarification.

Once that it was determined that suspended solids could be removed effectively by air flotation, it was simultaneously learned that BOD was dissolved, thus requiring bio-oxidation for its removal.

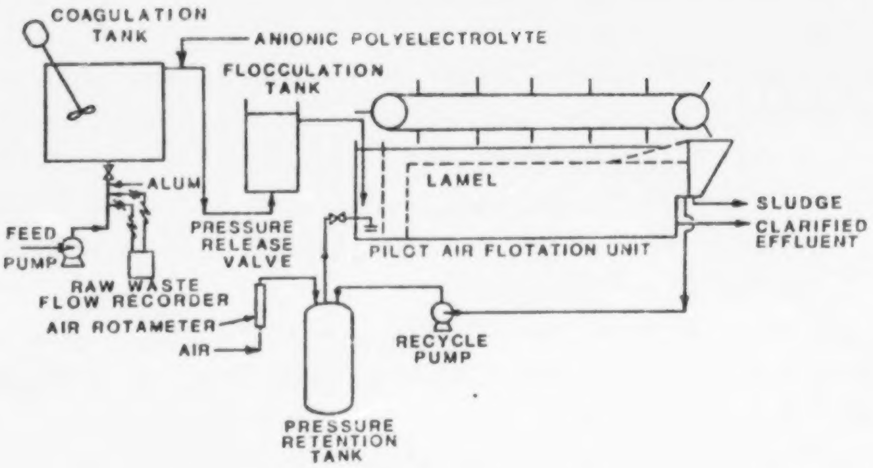
COAGULATION TANK
ANIONIC POLYELECTROLYTE
FLOCCULATION TANK
LAMEL
ALUM
SLUDGE
CLARIFIED EFFLUENT
FEED PUMP
PRESSURE RELEASE VALVE
PILOT AIR FLOTATION UNIT
RAW WASTE FLOW RECORDER
AIR ROTAMETER
AIR
RECYCLE PUMP
PRESSURE RETENTION TANK

Figure 1. Air flotation unit.

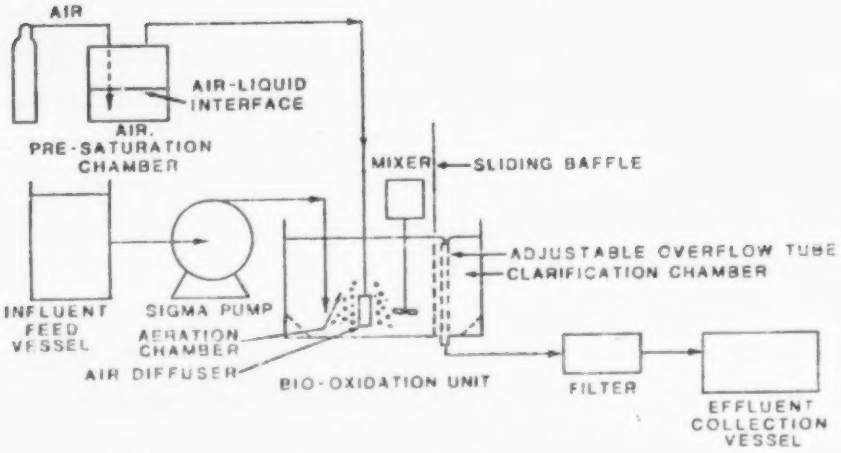
AIR
AIR-LIQUID INTERFACE
AIR
PRE-SATURATION CHAMBER
MIXER
SLIDING BAFFLE
ADJUSTABLE OVERFLOW TUBE
CLARIFICATION CHAMBER
INFLUENT FEED VESSEL
SIGMA PUMP
AERATION CHAMBER
AIR DIFFUSER
BIO-OXIDATION UNIT
FILTER
EFFLUENT COLLECTION VESSEL

Figure 2. Laboratory bio-oxidation unit.

In order to determine the biodegradability of the combined wastewater, composite wastewater samples were tested to affix toxicity, nutrient requirements for biological stabilization, oxygen requirements, oxygen uptake rates at various organic loadings, BOD_5 loading ratio, and retention time necessary during aeration.

Mixtures of wastewater and activated sludge from a sewage treatment plant were aerated with a gradual concentration increase of plant wastewater over a 2-week period until 100 percent of the wastewater under aeration was plant wastewater exclusively. The acclimated organisms were used as seed material in five 2-liter aerated lagoon units, each equipped with mixers.

Nutrient fortification of the wastewater was stopped once analysis showed that sufficient amounts of nutrients were inherently present already.

Wastewater was continuously fed into laboratory units, varying retention times between 1 and 5 days and temperatures between 5° C and 15° C. A Warburg respirometer measured typical oxygen uptake rates of 2.6 mg/l per hour and would have indicated the presence of toxic materials if they in fact had been present.

Other results concluded that (1) retention times of more than 1 day could lead to underloading and autooxidation, (2) loading ratios from 0.20 to 0.50 pounds BOD_5 per pound of mixed liquor suspended solids (MLSS) per day provided excellent effluent quality (figure 3), and (3) a BOD_5 removal of 90 percent was possible using a completely mixed aerated lagoon (figure 4).

However, coincident with this BOD_5 reduction was a three-to-five-fold increase in suspended solids during biological oxidation.

Once the choice of a dissolved air flotation system is made, six major variables must be studied and, if possible, optimized. These are: (1) chemical feed rates; (2) air/solids ratio; (3) retention time; (4) recycle ratio; (5) pressurization of recycle stream; and (6) loading rate. Meaningful answers for each of these categories require the use of a pilot unit; the one chosen offered a 15-gpm capability.

An optimum chemical feed rate will produce some level of clarity. Excesses increase turbidity, while a lower rate reduces suspended solids

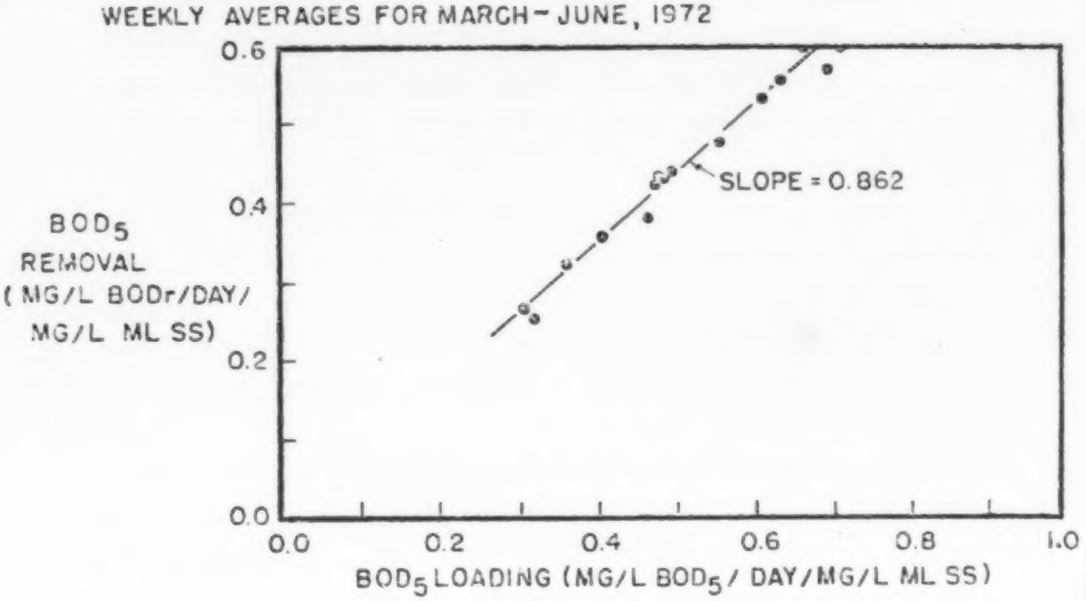

Figure 3. BOD_5 removal vs. BOD_5 loading for aerated lagoon.

removal. Alum dosages of 30-150 mg/l and flocculent aid dosages of 0.25-1.0 mg/l offered the ranges to be tried and optimized in the fullscale unit.

An air/solids ratio represents a potential to float all of the suspended matter. Excess air may, in some cases, adversely affect effluent quality. With wide fluctuations of influent solids, an air/solids ratio must also vary accordingly. For a recycle rate of 33-1/3 percent and a loading rate of 5.0 gpm/ft^2 , an average ratio of 0.114 lb air/lb solids was used during pilot trials.

The retention times in the pressurization system and in the flotation unit must be balanced. While a long retention time insures maximum air saturation and flotation of particles with low separation velocities, excess retention time limits air-bubble life and permits float dissociation.

Recycle rate of 20 percent gave consistent good results, but with the onset of turbulence at about 33-1/3 percent indicated that a maximum had been reached (figure 5).

Recycle pressurization improves clarifier performance with higher

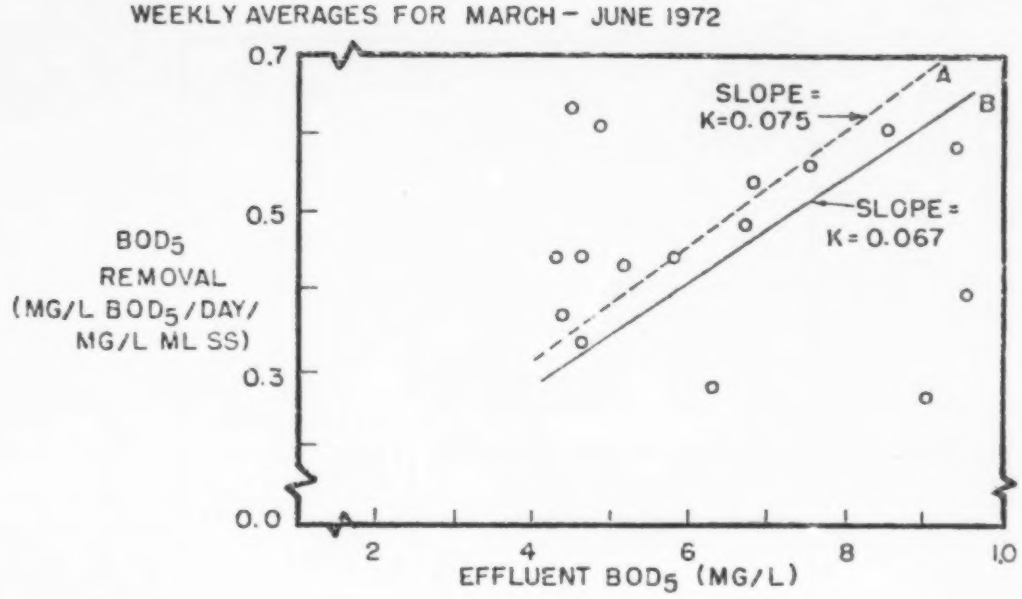

Figure 4. BOD_5 removal vs. effluent BOD_5 - removal rate coefficient for aerated lagoon.

pressures being limited by economics and tolerated to the point where bubble size and turbulence are controlled, usually within the 40-60 psig range.

In order to increase the loading rates without producing turbulent flow, the use of lamels (parallel vertical baffles) produced two specific effects; a reduction in turbulence and backmixing, and a surface quieting where particles can rise for skimming without excessive interference caused by flow across the unit.

The lamel concept is based on the dimensionless Reynolds Number:

$$N_{Re} = \frac{4R_h G}{M} \quad .$$

This relates mass velocity, G, in an open channel to its hydraulic radius, R_h, and the viscosity, μ, of the liquid.

This is accomplished by choosing a $N_{Re} < 2000$ and assuming the viscosity to be constant, leaving only the variables of mass velocity and hy-

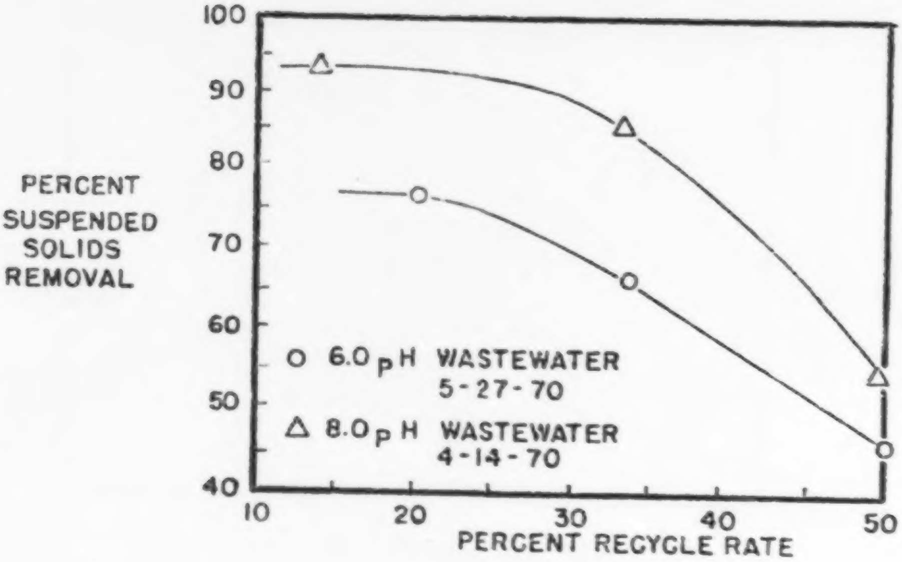

Figure 5. Percent suspended solids removal vs. percent recycle rate for pilot air flotation clarifier.

draulic radius. By dividing the flotation chamber into a series of narrow channels called lamels, dramatic increases in the loading rate (mass velocity) can be realized (ref. 2).

Each step of the treatment process would add a chemical to coagulate or condition the suspended solids to a point where it could be segregated or isolated from the mainstream of the wastewater flow. However, any treatment process, such as chemical coagulation with biooxidation, is one of displacement, i.e., the contaminants are isolated from the water stream but now become a solid waste disposal problem (figure 6). As an example, at a loading rate of 5.0 gpm/ft^2 and a recycle rate of 33-1/3 percent, sludge rates averaged 0.28 gpm. Average concentration of the sludge was 4.11 percent total solids by weight and 42.3 percent volatile content based on dry solids content. Sludge total solids varied between 1.47 and 7.43 percent. By extending these numbers, a full-scale primary unit would generate a projected sludge of 25,375 gallons/day or 4½ tons dry solids/day. The

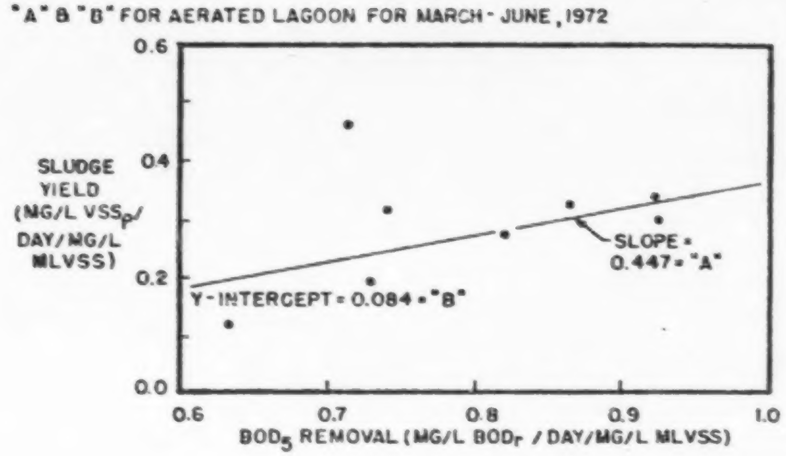

Figure 6. Sludge yield vs. BOD removal - determination of biological oxidation constants.

sludge generated from this treatment can take many steps as simple screen drying, centrifugation, vacuum filtration, and pressure filtration.

The first attempt by means of a sludge drying bed accomplished a minimal amount of dewatering; however, it proved to be unsuccessful due to sludge stratification and screen blinding in a short period of time. Under ordinary circumstances, centrifugation would have offered a viable solution; however, in the case of suspended rubber solids where the sludge is actually lighter than water, effective separation could not be obtained. There are also other inherent plugging problems with rubber particles. Vacuum filtration using a rotary drum offered little further improvement, for filtration rates were extremely slow.

Pressure filtration, however, was considered to have shown the most promise because relatively dry filter cake of 50-65 percent solids could be obtained. Typical conditions for a horizontal plate and frame filter indi-

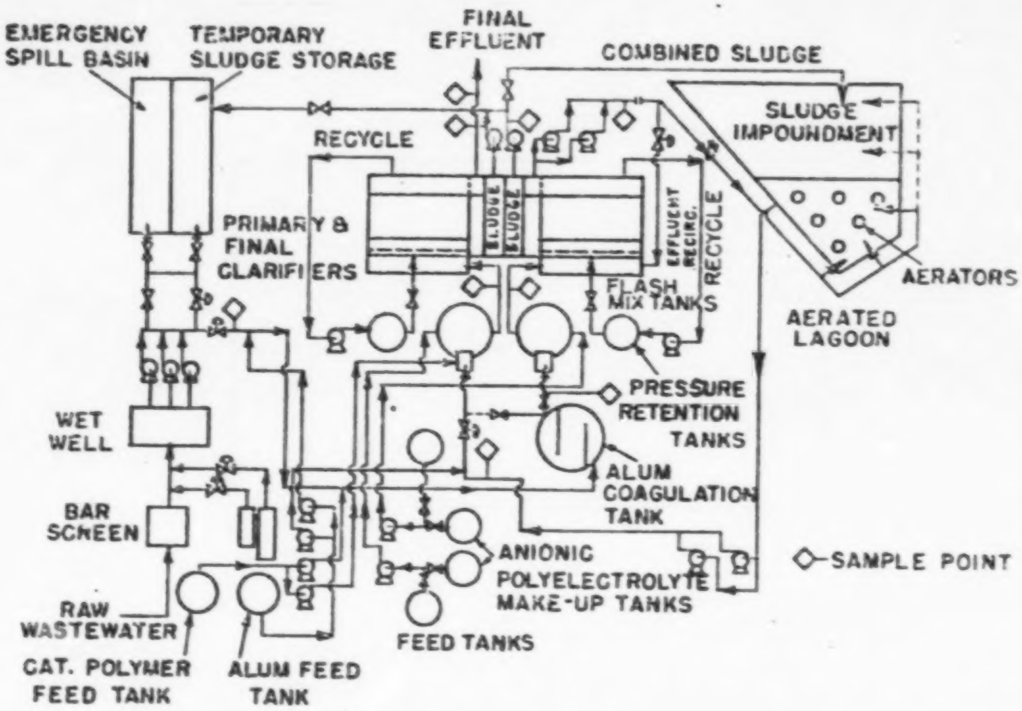
EMERGENCY SPILL BASIN
TEMPORARY SLUDGE STORAGE
FINAL EFFLUENT
COMBINED SLUDGE
SLUDGE IMPOUNDMENT
RECYCLE
PRIMARY & FINAL CLARIFIERS
SLUDGE
SLUDGE
EFFLUENT RECIRC.
RECYCLE
FLASH MIX TANKS
AERATORS
AERATED LAGOON
PRESSURE RETENTION TANKS
WET WELL
ALUM COAGULATION TANK
BAR SCREEN
ANIONIC POLYELECTROLYTE MAKE-UP TANKS
◇-SAMPLE POINT
RAW WASTEWATER
FEED TANKS
CAT. POLYMER FEED TANK
ALUM FEED TANK

Figure 7. Flow diagram of treatment plant.

cate that a sludge of 50 percent dry solids could be obtained on a 1.5-hour filtering cycle with 225 psi as its terminal filtration pressure. Because of its low operating costs, the filter-capacity-expansion high capital cost of pressure filtration was small considered over a long useful operating life.

TREATMENT FACILITIES

The general flow pattern of this treatment process is shown in figure 7. Description of the various stages begins with the raw wastewater flow through the bar screen, and pH adjustment follows just prior to alum coagulation of the suspended solids (figure 8). A cationic polyelectrolyte is added separate from the alum to avoid inhibiting mass transfer. The coagulation tank is divided into three compartments by baffles. Mixing is

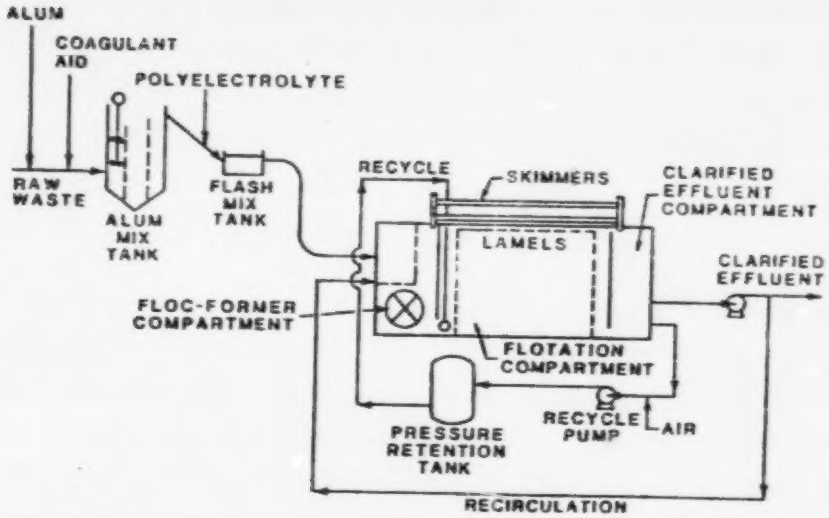
ALUM
COAGULANT AID
POLYELECTROLYTE
RAW WASTE
ALUM MIX TANK
FLASH MIX TANK
RECYCLE
SKIMMERS
CLARIFIED EFFLUENT COMPARTMENT
LAMELS
CLARIFIED EFFLUENT
FLOC-FORMER COMPARTMENT
FLOTATION COMPARTMENT
PRESSURE RETENTION TANK
RECYCLE PUMP
AIR
RECIRCULATION

Figure 8. Primary air-flotation clarifier.

necessary in the first section, quiescence in the remaining two to permit the floc to grow. Wastewater passes through a flow-measuring box where anionic polyelectrolyte is added as the wastewater enters a flash-mixing tank. Flow then is uniformly distributed into the floc-former compartment of the primary flotation clarifier unit. The primary clarifier effluent is pumped to the aerated lagoon for biooxidation. After a 24-hour retention period, the lagoon effluent is pumped back to the final clarifier where alum is added en route and cationic polyelectrolyte is added within the flow-measuring box. Anionic polyelectrolyte is introduced at the flash-mixing tank just prior to the flow entering the final clarifier via distribution flume. The final clarifier effluent is discharged to a concrete-lined trench before leaving the plant property.

Sampling

Throughout the plant there are located nine major sampling points. Of these, three different sampling methods are used; namely, continual, automatic composite, and a grab sample on 6-hour intervals composited over a 24-hour period. The influent raw water to the bar screen and the final effluent to the bayou are under composite sampling. This method is also used to monitor the effluent from the primary clarifier and the effluent from the aeration lagoons. Grab samples are taken at five locations: (1) equalized raw water to mix tank #1, (2) feed to primary clarifier, (3) feed to final clarifier, (4) sludge from primary clarifier, and (5) sludge from final clarifier.

System Performance

Problems which interfered with smooth continued operation centered around the clarifiers with turbulence and sludge accumulation. High air suction from the flash-mixing tank preceding the clarifiers caused turbulence, resulting in floc breakup and required higher-than-anticipated chemical dosages. Liquid-level controllers have since helped maintain a sufficient inventory of water and eliminate air suction.

Sludge would inevitably accumulate in the bottom of the clarifiers due to the continual presence of carbon black and its high specific gravity. Even though both air flotation clarifiers have bottom sludge blow-down headers inside the sludge collection troughs and the sloped floors toward the trough outlet, downtime for cleanout could not be avoided. A 6- to 10-hour period using a firehose was needed for a cleanout.

During the 9-month demonstration period, downtime was 5.2 percent of the total operating time for the primary and 4.1 percent for the secondary. One primary clarifier would always be 100 percent operational because the dissolved air is also interconnected with the secondary clarifier, allowing it to function if and when the primary clarifier was down for maintenance or cleanout.

Performance shown by table 1 demonstrates the overall removal efficiency and effluent discharge concentrations.

A further comparison can be made by looking at Federal Effluent Guidelines (table 2), which relate allowable concentration limits of characteristic parameters to raw material usage and/or product output.

Table 1. System performance

Flow - 3.55 MGD				
Parameters	Effluent	Limit	Target	Percent Removal
pH	7.1	7.0 ± 0.5	7.0	---
Suspended solids*	29	25	10	88*
BOD	8	10	7	89
COD	78	135	---	84
Dissolved oxygen	5.2	4.0	(65% of Saturation)	---
Oil & grease	3.2	7.5	Nil	83
Chromium (+3,+6)	0.05	0.05	Nil	100
Phenol	0.03	0.05	Nil	77

Table 2. Federal EPA effluent guidelines synthetic rubber production

Parameter	Actual	Guideline limit (mg/l)	
COD	1.12	6.38	(398)
BOD	0.11	0.40	(25)
Suspended solids	0.45	0.65	(40)
Oil & grease	0.05	0.16	(10)

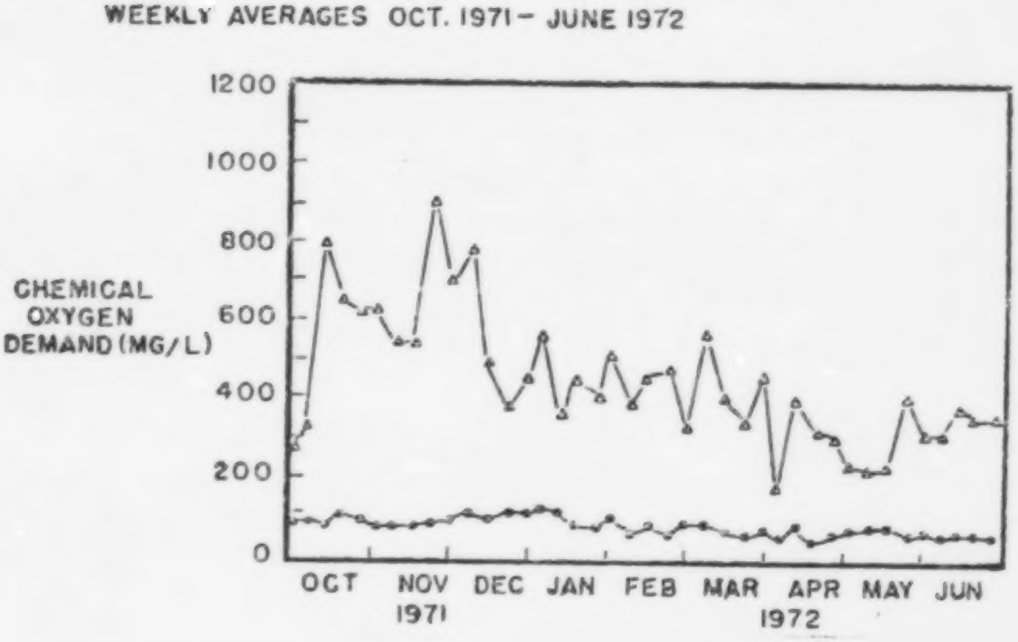

Figure 9. Influent and effluent chemical oxygen demand.

The parameters designated by the EPA for the synthetic rubber industry are chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), suspended solids (SS), and oil and grease.

Figures 9, 10, and 11 graphically give a broad impression of influent versus effluent for COD, BOD_5, and SS during the demonstration period, October 1971 - June 1972.

Figures 12 and 13 indicate that system performance is not reflected by percent solids removal across each air flotation clarifier. It must be remembered that biooxidation occurs between clarifiers reintroducing new suspended solids that are to be removed during secondary clarification. A comparison of chemical usage in each clarifier suggests an approximately equal removal of suspended solids (table 3). The scattering of data suggests the influence of these and other operational variables as discussed previously in Theoretical Considerations.

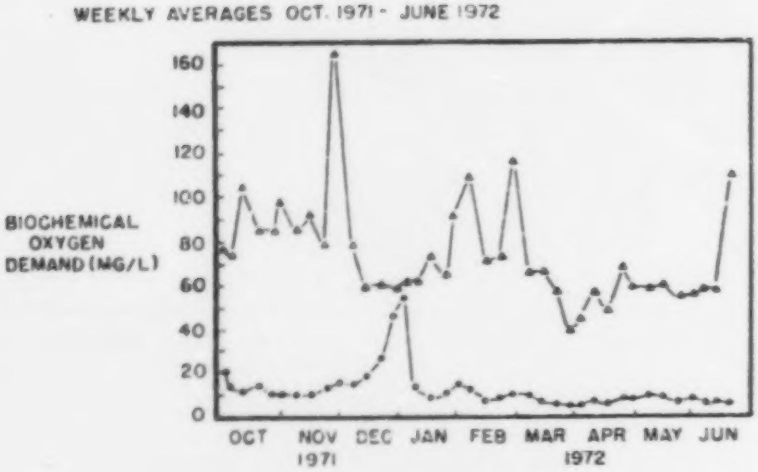

Figure 10. Influent and effluent biochemical oxygen demand.

FINANCIAL CONSIDERATIONS

The total cost, including engineering, of this wastewater treatment facility was $1,472,528. The engineering costs included survey work, water testing, pilot plant testing, plans and specifications, quotes and bid preparation, and supervision and inspection of construction. The increased costs incurred in excess of those expected for similar facilities were a result of (1) the great distances between the aerated lagoon and clarifiers requiring a lift station, added pumping capability, and two electrical substations, and (2) anticipated high chemical costs that suggested more extensive instrumentation.

The total operating and maintenance cost during the 9-month demonstration period was $367,274, which includes $57,404 for contract sludge disposal. Since sludge was disposed of by a contractor for only 5½ months, the expected annual cost of sludge disposal, $125,245, was not realized (table

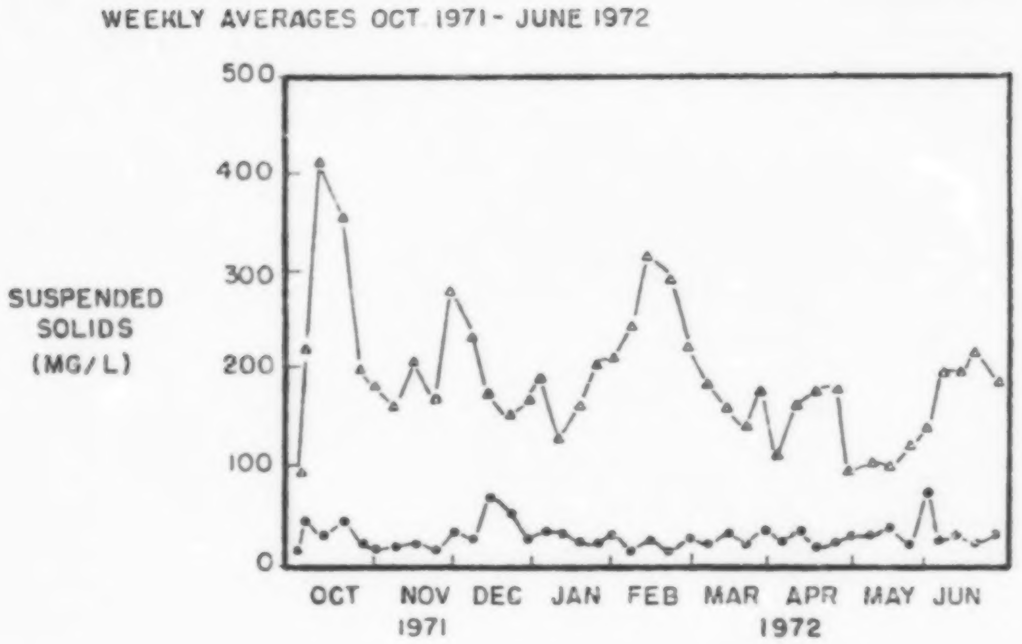

Figure 11. Influent and effluent suspended solids.

4). The sludge is presently being impounded until a more desirable means of disposal is developed.

SUMMARY AND CONCLUSIONS

The wastewater treatment facility at Firestone Synthetic Rubber & Latex Company's Lake Charles, Louisiana, plant was studied for a 9-month period from October 1, 1971 through June 30, 1972. The following conclusions were reached based on the results of the study presented in this report.

1. A completely mixed aerated lagoon was an effective and acceptable means of removing oxygen-consuming pollutants from the wastewater, as shown by an average BOD_5 removal of 84.2 percent.

2. Dissolved air flotation removed 85.2 percent of suspended solids and was the only effective method to produce a high-quality effluent.

3. Only chemical treatment of the wastewater could remove colloidal materials and provide an effective floc for initial and final dissolved air-flotation clarification.

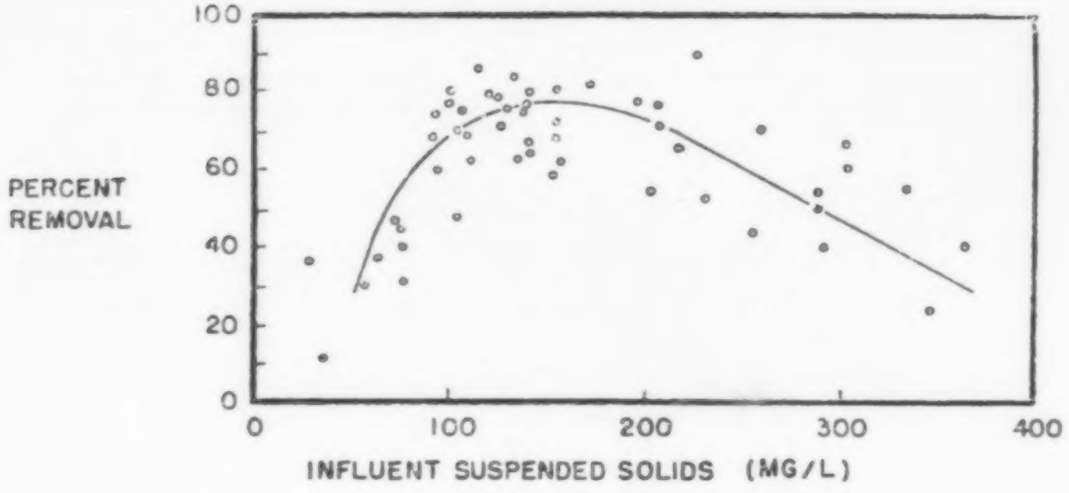

Figure 12. Percent removal vs. influent suspended solids for primary clarifier (May & June, 1972).

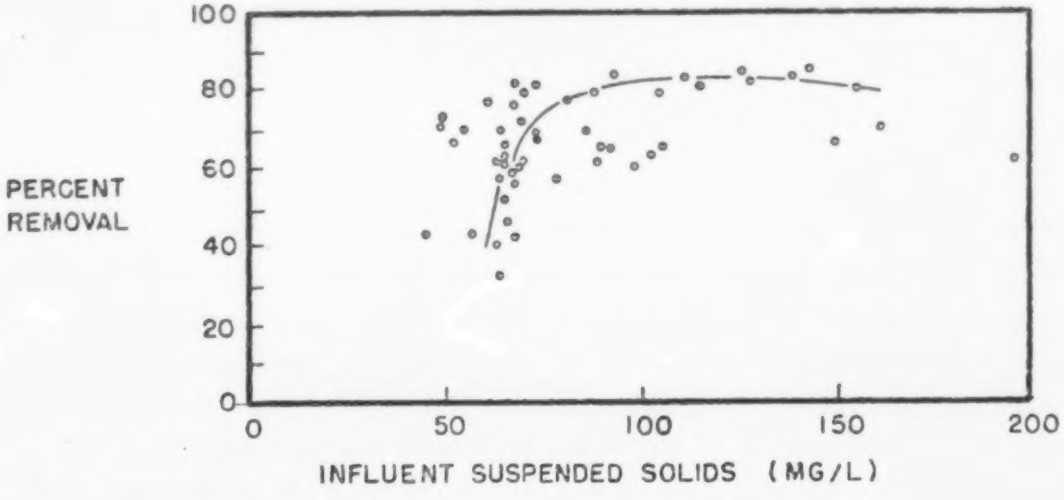

Figure 13. Percent removal vs. influent suspended solids for secondary clarifier (May & June, 1972).

Table 3. Chemical feed rates*

	Primary Clarification			Secondary Clarification		
Month	Alum	Cat. polymer	Anionic polymer	Alum	Cat. polymer	Anionic polymer
1971						
Oct.	20	4.6	0.79	58	3.8	0.82
Nov.	44	2.6	0.76	36	2.4	0.75
Dec.	62	1.5	0.85	58	1.8	0.89
1972						
Jan.	52	0.0	0.63	57	0.0	0.62
Feb.	20	2.8	0.73	33	4.7	0.61
Mar.	40	5.4	0.70	29	4.8	0.57
Apr.	37	4.7	0.70	27	3.8	0.53
May	29	3.6	0.61	24	3.2	0.49
June	30	3.6	0.70	34	3.1	0.53
Average	37	3.2	0.72	40	3.1	0.65

*Data represent daily average concentrations as mg/l based on total wastewater flow.

4. Final dissolved air-flotation clarification was required to produce a high-quality effluent and to prevent sludge autooxidation.

5. Turbulence within the chemical coagulant and precipitation treatment system hindered solids removal during clarification and increased the amount of chemicals required to sustain an effective floc formation.

6. Cleaning of the primary clarifier was necessary every 4 to 6 weeks due to the accumulation of solids. The final clarifier only required cleaning every 10 to 12 weeks due to the solids concentration of the lagoon effluent and to the nature of the effluent solids. The accumulation of solids forced the cleaning of the primary clarifier every 4 to 6 weeks; the final clarifier every 10 to 12 weeks.

Table 4. Total annual costs

Item	Annual cost
Interest on capital cost of $1,472,528	$ 51,538
Annual operating and maintenance cost	409,751
Estimated equipment replacement and depreciation	147,253
TOTAL ANNUAL COST (excluding sludge disposal costs)	$ 608,542
Sludge disposal costs	$ 125,245
TOTAL ANNUAL COST (including sludge disposal costs)	$ 733,787

7. Carbon black particles present in the wastewater hindered floc formation and float stability during air flotation, requiring higher alum dosages for effective clarification.

8. The best environment for effective clarification required a pH adjustment of the raw wastewater to a 6.5-8.0 range.

9. The average substrate removal rate coefficient (k) was found to be 0.067 1/mg-day, indicating that the wastewater was amenable to rapid biological oxidation.

10. A retention time of approximately 1 day in the aerated lagoon produced maximum BOD reductions. Longer retention times resulted in lower BOD removals due to relatively low organic loading ratios and sludge auto-oxidation.

11. Sufficient concentrations of nitrogen, phosphorus, and other essential nutrients were present in the wastewater to support biological activity without supplemental addition.

12. The ambient air temperature had little effect on aerated lagoon performance. The relatively short stabilization period and the temperature of the raw wastewater maintained adequate lagoon temperatures for efficient lagoon operations all year long.

13. The average sludge generation was 6.34 gallons/1,000 gallons of wastewater treated.

A number of problems inherent in this system should be considered in order to improve its overall operation, namely: (1) better equalization to improve pH adjustment to effect a reduction in chemical costs incident to alum coagulation; (2) the addition of drag-out equipment in the flotation compartment of the primary clarifier to reduce downtime for cleanup; (3) reinforcement of lagoon walls to prevent erosion: and (4) rectangular shaping of lagoons to develop good mixing, flow, and oxygen-transfer patterns and to avoid short-circuiting and solids accumulation in stagnant areas.

It has been demonstrated that wastewater generated from synthetic rubber production can be effectively treated using a multifaceted approach, which includes coagulation, air flotation, biooxidation, and sludge dewatering.

ACKNOWLEDGMENTS

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Special gratitude is given to Messrs. A. H. King, J. Ogea, and J. W. Sutton for the actual performance of this development study and to other people of the Firestone Synthetic Rubber & Latex Company, Messrs. T. E. Salisbury, J. R. Swenson, M. W. Carlson, and P. A. Boley, who were instrumental in this project.

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DISCUSSION

MRS. JAMES H. ANGEL (Citizens for Land and Water Use, Cleveland Metropolitan Area, Cleveland, Ohio): Are the domestic waste-treatment plants, secondary treatment plants, often interrupted by batch doses of pollutants that knock out bacterial treatment? I want to know if your system of bacterial treatment is susceptible to being interrupted.

MR. TROPPE: By our own batch dose?

MRS. ANGEL: Yes?

MR. TROPPE: No. Discharge to the sewage plants would be separate. Again, this is the advantage of keeping your storm water and domestic wastes and process wastes separate. As a case in point, the city of Akron has allocated, as we do on our design, separate ducts. Let us say one of the rubber companies happened to have a "batch dump." Most of these guys are conscientious, not unscrupulous; they would call up the sewage treatment plant and say, "We just dumped, by accident naturally, 500 gallons of latex." So by the time it gets down to the City of Akron (Treatment Works) they are ready for it.

MRS. ANGEL: They can sidetrack it?

MR. TROPPE: Yes, to holding basins for specialized treatment at a later time.

MRS. ANGEL: Why do your bacteria eat each other? I don't think that they do that in domestic waste. Is it some kind of a monster strain?

MR. TROPPE: It is a strange love affair, yes. I didn't quite understand that, but we will have to pursue this further.

12 March 1975

Session II:

CHEMICALS AND THEIR EFFECTS

William E. McCormick*
Session Chairman

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*Managing Director, American Industrial Hygiene Association, Akron, Ohio.

TOXICOLOGY OF ACRYLONITRILE

C. Boyd Shaffer, Ph.D.*

Abstract

Acrylonitrile is a colorless, volatile liquid with a faintly pungent odor. Its vapor pressure at room temperature is 100 torr, the specific gravity is 0.81, and the boiling point at 760 torr is 77.3°C. From its initial synthesis in 1893, it remained a laboratory curiosity until the need for oil-resistant rubber for military purposes stimulated commercial production during World War II. The big impetus to commercial production, however, was the development of acrylic fibers in the early 1950's. Of the 1,400 million pounds of acrylonitrile produced in 1973, synthetic fibers consumed more than half. Nitrile rubber required less than 5 percent of 1973 production.

Apart from some relatively trivial uses as a fumigant and chemical intermediate, acrylonitrile is used almost entirely in the manufacture of copolymers. It can be copolymerized with a large number of vinyl monomers using a variety of techniques. Its introduction into copolymers imparts a wide range of improvements in the properties of the final product.

Acrylonitrile has a somewhat lower order of acute toxicity than might be inferred from its chemical structure. The single oral dose LD50 for male albino rats is about 80 mg/kg, and that for female rats is of the same order of magnitude. Rats will withstand a 1-hour exposure of 1,000 ppm or a 4-hour exposure to 500 ppm with little apparent effect. The single dose LD50 for rabbits by 24-hour skin contact is less than 200 mg/kg, but this result is achieved only because the dose is prevented from evaporating by an impervious wrapping about the animal. Acrylonitrile is a primary irritant to rabbit eyes and skin, and will cause severe blisters on human skin if held in contact under clothing, particularly footwear.

The controversy over whether acrylonitrile exerts its acute toxic action through the liberation of cyanide ion has not yet been fully resolved, although the cyanide antidotes are customarily recommended for

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*Director of Toxicology, American Cyanamid Company, Wayne, New Jersey 07470.

cases of intoxication. It seems reasonable to conclude that the acute effects are attributable only in part to the release of inorganic cyanide.

The Threshold Limit Value of 20 ppm of vapor of acrylonitrile has not changed since it was proposed in 1945. The value was set partly on the basis of animal exposures and partly by analogy with the 10 ppm value for hydrogen cyanide. Industrial health experience with acrylonitrile in the United States has been uniformly good, although episodes of transient clinical illness were reported shortly after introduction of its use in rubber manufacture. Long-term feeding studies with rats support a conclusion that it is not carcinogenic.

Results of more extensive studies, some completed and some about to be undertaken, will be available in the near future.

Acrylonitrile is a colorless, volatile liquid with a faintly pungent odor. Its vapor pressure at room temperature is 100 torr, the specific gravity is 0.81, and the boiling point at 760 torr is 77.3°C. It was first synthesized in 1893 by Moureu by the removal of water from ethylene cyanohydrin, or acrylamide, by reaction with phosphorus pentoxide.

Acrylonitrile achieved no significant commercial uses until the outbreak of World War II, when the demand for oil-resistant rubber for military purposes stimulated commercial production. By that time it had been discovered that in order to effect decomposition of ethylene cyanohydrin into acrylonitrile and water, it is not necessary to remove the evolved water by the use of a dehydrating agent such as phosphorus pentoxide. The decomposition of the cyanohydrin proceeds spontaneously and rapidly in the presence of suitable catalysts and under the proper conditions. The wet acrylonitrile that is produced may be dried by azeotropic distillation, either by itself or with dichloromethane or chloroform.

Acrylonitrile is also formed when a mixture of acetylene and hydrocyanic acid is passed over the proper catalysts at 400°-500°C.

Both the cyanohydrin process and the acetylene process have been used commercially for the production of acrylonitrile. Now, however, all acrylonitrile is manufactured by the catalytic ammoxidation of propylene. In this process, liquid propylene and ammonia are vaporized and fed with air to a fluidized-bed reactor. The reactor effluent gases are cooled, excess ammonia is neutralized, and the soluble organic products are absorbed in a circulating water recovery system. Crude acrylonitrile and hydrocyanic acid are recovered from the water system by azeotropic extractive distillation. The crude acrylonitrile-hydrocyanic acid mixture is subsequently separated into its components and purified in a series of three distillation columns.

Apart from some relatively trivial uses as a fumigant and some minor uses as a chemical intermediate, acrylonitrile is used almost entirely in the manufacture of copolymers. Despite the remarkable properties which acrylonitrile imparts to rubbers, the production of rubber goods is not an important end use of the compound. Only about 4 percent of the 1973 production of acrylonitrile was used in the manufacture of rubber. The rubbers are usually made from acrylonitrile-butadiene copolymers, which contain 15-55 percent of acrylonitrile. These rubbers possess high resistance to the swelling action of solvents, oils, and greases, far surpassing natural rubber or GR-S products in this respect. In addition, they possess excellent resistance to heat, aging, and sunlight. Depending upon the methods of compounding, a great variety of rubbers characterized by high tensile strength, excellent elongation, and low-compression set can be produced.

The development of acrylic fibers in the early 1950's provided the big impetus to commercial production of acrylonitrile. Today, acrylic fibers are by far the largest end-use consumer of acrylonitrile, representing more than half of the 1973 demand. ABS plastics and barrier resins, both high in acrylonitrile content, represent the fastest growing use at present. Production of acrylamide, for which acrylonitrile is the raw material, is expected to grow substantially in the coming years.

There are currently four producers of acrylonitrile in the United States: Monsanto, du Pont, Vistron, and Cyanamid. The total production by these four in 1973 was 1,450 million pounds.

Investigation of the toxicology of acrylonitrile was begun promptly after development of commercial interest in the compound. In 1942, Dudley and Neal (ref. 1) reported the results of single exposures to vapor. They found a wide range in susceptibility among the various species studied, with guinea pigs showing a marked resistance to the acutely lethal effects of the compound, and dogs succumbing to concentrations that had but slight effect on the other species. They also noted that the signs of toxicity in all species, except guinea pigs, were similar to those of cyanide intoxication, and speculated that the mechanism of the toxic action of acrylonitrile was cleavage of the molecule to yield hydrogen cyanide. The additional observation that sodium nitrite by intravenous injection had a protective and antidotal effect tended to support this hypothesis.

Subsequently in 1942, Dudley et al. (ref. 2) published the results of repeated, daily exposures of monkeys, rats, guinea pigs, rabbits, and cats to vapor of acrylonitrile. The animals were exposed for 4 hours daily, 5 days per week, for 8 weeks. The Threshold Limit Value of 20 ppm suggested by the authors as a result of this work has remained unchanged.

In our own laboratories, we have performed acute toxicity and eye and skin irritation tests according to the procedures that are described in the regulations to the Federal Hazardous Substances Act, which are substantially those commonly employed in most industrial and contract toxicology laboratories. We determined that the single oral dose LD50 for male albino rats is approximately 80 mg/kg, and that female rats survive an oral dose of 50 mg/kg. Furthermore, rats are not killed by a 1-hour exposure to approximately 920 ppm (2 mg/l), although two of six animals succumbed to a 4-hour exposure to about 460 ppm (1 mg/l). A dosage of 200 mg/kg is lethal to rabbits within 6 to 24 hours after application to the shaved skin under an impervious covering that prevents evaporation. I mention these experiments chiefly because they include the three components of the statutory (FHSA) definition of "highly toxic." Therefore, acrylonitrile is "highly toxic" by skin absorption and is customarily labeled as a "poison," although there seems little doubt that the compound would not cause death at the indicated dosage if it were not retained in contact with the skin by rather stringent means.

Acrylonitrile is an irritant to rabbit eyes and rabbit skin in the conventional tests. Destruction of tissue is not observed under these conditions; hence, the compound is not considered to be a "corrosive."

The relative rarity of acute illness from exposure to acrylonitrile is remarkable in view of the LD50 and LC50 values and the considerable amounts of the product that are manufactured and used. No fatalities are known to have occurred, at least in the United States. Serious degrees of exposure to vapor are not likely to occur under the usual conditions under which the product is handled. Most cases of systemic intoxication by inhalation of vapor have been mild, and commence during the actual exposure with such symptoms as eye irritation, nausea, headache, and sneezing. Other symptoms that may occur include weakness, lightheadedness, and vomiting. Termination of the exposure at this point results in rapid improvement, with no known residual disability.

Systemic intoxication by skin contact has rarely, if ever, been observed occupationally, probably because acrylonitrile evaporates from the uncovered skin before toxic quantities can be absorbed. However, one extremely hazardous aspect of contact cannot be overemphasized. Clothing wetted with acrylonitrile should be removed immediately, and should not be worn again until thoroughly laundered. The reason for this is not only avoidance of absorption but also the prevention of blister formation. The most characteristic effect occurs on the feet, since acrylonitrile is easily absorbed in shoe leather. This hazard is present when a workman walks through a spill on the floor or when the material is splashed on a shoe. Unless the shoe is removed at once and the foot washed, large blisters will appear on the foot after a latent period of several hours. Usually there is little or no pain or inflammation. Otherwise, the blisters resemble extensive second-degree thermal burns.

Reports of adverse effects from occupational exposure to acrylonitrile have been very few. Wilson (ref. 3) in 1944 described several cases of mild jaundice among workmen engaged in handling of the compound. He found these individuals frequently exhibiting symptoms of vomiting, nausea, and weakness, with headache, fatigue, and diarrhea present. In some cases nasal and an upper respiratory oppressed feeling was noted.

No further clinical reports of possible cumulative effects appeared in the literature until 1972 when Sakurai and Kusumoto (ref. 4) published the results of an epidemiological study of acrylonitrile workers in Japan. A total of 576 workers from five synthetic fiber plants were examined over a 10-year period with respect to certain symptoms and certain objective tests. The workers were divided into several brackets with respect to age, levels of exposure, and length of exposure. The conclusion was that the incidence of subjective complaints as well as the incidence of abnormal values of some of the tests related to liver function increased in relation to the length of exposure to acrylonitrile. These incidences were found to be higher at the higher level of exposure.

In striking contrast to the early report by Wilson and the more recent account by the Japanese authors, has been the uniformly good health experience of U.S. manufacturers and users of acrylonitrile. It has been our experience in this Company that there have been no cases of liver dysfunction secondary to exposure to acrylonitrile; indeed, there has been no subacute or chronic illness of any variety that could be linked to exposure to the compound. Jaundice has not occurred, nor have there been subjective complaints of fatigue, debility, or loss of appetite. In our professional contacts with medical personnel of other manufacturers and users, we have been advised that they have observed nothing that would corroborate the conclusions of the Japanese study.

A review and comment upon all of the numerous animal feeding and inhalation tests of acrylonitrile that have appeared in the literature would exceed the time allotted to this presentation. Two studies, however, deserve special mention because of their duration. The first, performed by Svirbely and Floyd is available, unfortunately, only in abstract form (ref. 5); the complete study was never published, and the details appear to be lost. The abstract stated the following conclusions:

"1. Histopathological examination has not shown significant pronounced effects in the organs and bone marrow smears of rats given 0.5, 5, and 50 ppm of acrylonitrile . . . in their drinking water for a 2-year period.

"2. Dogs are able to tolerate levels of acrylonitrile . . . around 500 ppm in their food, but levels of 1,000 ppm induced vomiting and loss in appetite.

"3. Reproduction studies in rats given . . . (acrylonitrile) at levels of 10, 100, and 500 ppm in their drinking water, have given some indication of a decrease in the indices of fertility, gestation, and viability at the highest level of acrylonitrile administered; a demonstrable muscular incoordination of the hind limbs was also unexpectedly observed in the female rats on the 500 ppm acrylonitrile level, following the weaning of the second litter."

A second long-term study has been reported by Tullar (ref. 6), although again the complete study was never published. In this investigation, which included only male rats, one group of animals was supplied with drinking water containing 0.05 percent by volume of acrylonitrile, while a second group received food that was fumigated with acrylonitrile by a standard procedure. Suitable analyses had established that food fumigated in that manner contained 38 mg/kg of acrylonitrile. Administration of the treated food and water was continued for 2 years. The animals that received acrylonitrile in the drinking water maintained a consistently lower mean weight than did the controls, and did not present the same thrifty appearance. Also, the survival rate was somewhat lower for that group than for the others. All of the animals that received acrylonitrile in the food survived the 2-year period, and had a growth rate equal to that of the controls.

On November 4, 1974, the Commissioner of Food and Drugs published in the Federal Register a proposed order to limit the amount of acrylonitrile monomer that could be extracted from acrylonitrile copolymers by food-simulating solvents, and to require further toxicological studies. The preamble to the proposal took account of both the Svirbely and Tullar studies noting that the possibility raised by Tullar that acrylonitrile may be a carcinogen "is unsupported because of the inadequacy of this study and the lack of a dose relationship. In addition, the fact that the tumors were of different kinds suggests no relationship to the agent fed." The preamble observed further, in reference to the Svirbely study, that "data from the study do have a limited usefulness in determining that there was no increased incidence of tumors in the animals administered acrylonitrile."

The results of two studies pertaining to the ingestion of acrylonitrile have just become available, and I am indebted to the Toxicology Research Laboratory, Health and Environment Research, of the Dow Chemical Company for permission to present a synopsis of these. In the first of these, acrylonitrile was administered to male and female dogs in the drinking water for 6 months at concentrations of 100, 200, and 300 mg/l. A majority of the dogs that received water containing 200 or 300 mg/l died or were sacrificed during the study, with the majority of the deaths occurring during the last 3 months. All of the dogs that died showed terminal depression, lethargy, weakness, and emaciation in conjunction with bronchopneumonia, which may have been indirectly related to ingestion of acrylonitrile. Among the dogs that received water containing 100 mg/l (8-10 mg/kg per day of acrylonitrile) no differences from controls were observed in survival, hematology, urinalyses, clinical chemistry, electrophoretic patterns of serum proteins, nonprotein sulfhydryl content of liver and kidney, and gross and microscopic appearance of organs and tissues. A slight increase in the mean relative weight of the kidneys of the males was observed, but this was considered to be of no significance.

In the second study, acrylonitrile was added to the drinking water of male and female rats over a period of 90 days in concentrations of 35, 85, 210, and 500 mg/l. The observations recorded included behavior, appearance, weight, food and water consumption, hematology, nonprotein sulfhydryl content of liver and kidney, clinical chemistry, urinalyses, organ weights, and gross and microscopic pathology. Water intake was significantly decreased at 500, 210, and 85 mg/l, but not at 35 mg/l. There was a lesser weight gain of males at the highest level, and of the females at the two higher levels. Small but significant increases in liver-to-bodyweight ratios were found in both sexes at the two higher levels. All other parameters evaluated were either comparable between the test and control groups, or the differences were considered to be unrelated to the ingestion of acrylonitrile. These results indicate that rats may drink water containing 85 mg/1 of acrylonitrile, equivalent to a daily dosage of 8-10 mg/kg, without harmful effect.

Additional long-term studies, involving exposure by both ingestion and inhalation, are in the design stage and are expected to be carried out under the joint sponsorship of a group of producers and users of acrylonitrile. Therefore, there is every likelihood that exhaustive information on the toxicology of the compound will become available over the next several years.

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DISCUSSION

OBSERVER: I was wondering how much of an air pollution problem this could be?

DR. SHAFFER: I am sorry, I don't think I have an opinion on air emissions of acrylonitrile, as a compounding problem with rubber. I do not have any information in that respect.

OBSERVER: Has there been any study on the synergistic actions of acrylonitrile with the chemicals in this area?

DR. SHAFFER: There are none that I am aware of. I can't think of any experiments in which acrylonitrile was administered in conjunction with another substance in this group to determine any joint action.

OBSERVER: In areas where there are multiple types of industries manufacturing plastics, this air pollution mix with acid is a very serious type of problem, and we desperately need studies of synergistic reactions. I wonder if you could carry the message some place where it would do some good.

DR. SHAFFER: I certainly shall. One of the points that the Food and Drug Administration wanted some information on was the possible synergistic reaction of acrylonitrile with cyanide. It is very likely that some experiments of that nature will be carried out. I agree with you that the possibility of adverse effects from interaction of various substances is a very important area. It is also quite complex in that it would be rather difficult to carry out studies in combinations in view of the wide variety of substances and the large number of combinations that could possibly occur. There are certain significant substances that should be investigated.

OBSERVER: There are two factors I want to mention. One is that high wind gusts and dust bring undiluted toxic elements. Also, there is the heat factor, which is possibly more concerned with the chlorinated hydrocarbons, but you have deterioration when it enters the home where it circulates through a furnace or contacts an electric heater or stove. So if the acrylonitrile is not faster in a tube, it would justify the settling of these mixes and the effect of heat in the home. I am sure that we have been struggling with this now for about 8 years. We need help on this air pollution problem. Thank you.

ALTERATION PRODUCTS OF SUBSTITUTED p-PHENYLENEDIAMINES

Henry C. Hollifield, Ph.D.
and Pasquale Lombardo*

Abstract

An investigation was conducted to determine the likelihood of the release of substituted p-phenylenediamines from rubber tires and their possible entry into the human food chain. Criteria for the selection of the amine antiozonants for study as possible food contaminants are given. The production volumes, end use, and waste disposal patterns of these products are discussed, and likely alteration products formed in the tire and in water are described.

Several years ago, the Food and Drug Administration instituted a Chemical Contaminants Program in the Bureau of Foods. A brief discussion of the program's objectives may help explain why industrial chemicals such as the substituted p-phenylenediamines were selected for study to determine the likelihood that they might enter the human food chain.

Over the past few years, there have been discoveries of methyl mercury contamination of fish and polychlorinated biphenyl residues in a variety of foods all over the world. These incidents of food contamination by industrial chemicals led to some tragic results for humans. Although never intended as food additives, mercury and polychlorinated biphenyls are examples of industrial chemicals that entered foods and caused illness and death.

In an attempt to prevent future disasters of this type, the Food and Drug Administration established its Chemical Contaminants Program. The program has two chief objectives. The first is to develop sufficient information to establish guidelines for recognized industrial chemical food contaminants. The second is to search for previously unrecognized industrial

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*Division of Chemical Technology, Bureau of Foods, Food and Drug Administration, 200 "C" St., S.W., Washington, D.C. 20204.

is indeed present in foods, it is then necessary to develop further information. The chemical's toxicity, level of occurrence in a variety of foods, and mode of entry into the food chain are vital information that must be determined to decide on an appropriate course of action.

In the search for unrecognized industrial contaminants, the above criteria are being applied to many different types of chemicals, including aromatic amines. It is well known that certain aromatic amines and/or their alteration products are carcinogenic or otherwise toxic to man or animals. As part of a project to investigate the possibility that aromatic amines enter the food chain, substituted p-phenylenediamines were selected as one of the types for further study. The following summarizes our investigation of the uses, reactions, and ultimate fate of these amines. Much of this information is abstracted from an internal FDA report (ref. 1).

Production of the substituted p-phenylenediamines presently exceeds 70 million pounds per year in the United States. Essentially all of this is used as antiozonants and antioxidants in rubber tires. The three basic types of p-phenylenediamines are shown in figure 1. They are the dialkyl, alkyl-aryl, and diaryl substituted products. In figure 1, R represents alkyl groups. It is estimated that N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine accounts for about 60 percent of all the p-phenylenediamines made, and N-phenyl-N'-sec-butyl and N,N'-bis-(1,4-dimethylpentyl) derivatives account for another 15 percent of the total production. These three particular compounds thus represent about 75 percent of all the p-phenylenediamines sold.

In general, based on the rubber content of the tire, the dialkyl p-phenylenediamine antiozonants are used at levels of about 1.5-2 percent, and the diaryl types at about 0.5 percent. It is obvious that large quantities of rubber waste are released to the environment as rubber dust and discarded tires. This broad exposure of the environment to large quantities of aromatic amine-containing waste could possibly result in the contamination of man's food chain by these chemicals. On the basis of production volume, end use patterns, and waste disposal patterns, the substituted p-phenylenediamines are considered to have high risk factors as possible food contaminants.

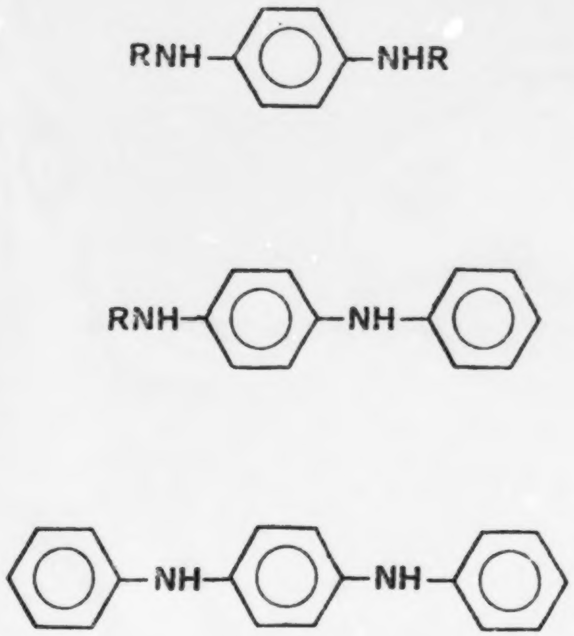

Figure 1. Examples of dialkyl, alkyl-aryl, and diaryl substitution.

On the other hand, the literature indicates that the bulk of these amines react both on the surface of the rubber tire, and also within the rubber. The amines react with substances such as ozone, oxygen, and vulcanization fragments (refs. 2,3). These reactions occur during manufacture, storage, and use of the product, and inert polymeric compounds are apparently formed by these reactions. This results either in the formation of protective films that are chemically bound to the elastomer surface, or in the formation of other reaction products that are chemically attached or physically retained within the vulcanizate. Very little is known regarding the identity of these polymeric alteration products.

Although most of the amines appear to remain within the rubber in one form or another, the literature indicates that small amounts of the free compound may be leached out by water (ref. 4). These amines may then ultimately be converted to alteration products which differ from those formed in tires. The amines apparently oxidize to their corresponding diimines, and are probably further altered by one or more competing reactions (ref. 5). For example, the oxidation of *p*-phenylenediamine will illustrate two possibilities of competing reactions. One type of reaction may predominate at

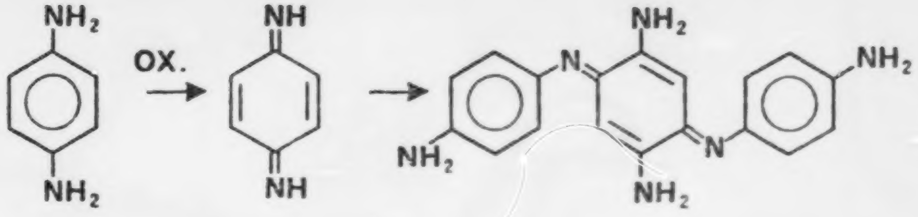

Figure 2. Formation of Bandrowski's Base.

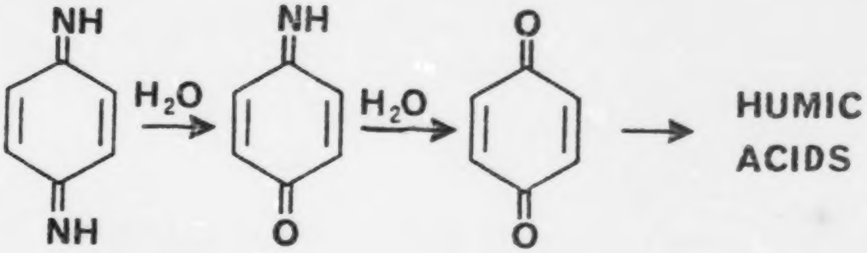

Figure 3. Hydrolysis of p-phenylenediimine.

high concentration and another at low concentration (ref. 6). First, when present in high concentrations and exposed to oxidizing conditions, p-phenylenediamine is converted to its diimine (see figure 2). This product in turn may couple with two unoxidized diamine molecules to produce a compound called Bandrowski's Base (shown on the right of figure 2). The coupling reaction rate is accelerated by increasing oxidant concentration, increasing pH, and increasing temperature. At low concentrations, however, the hydrolysis of the diimine predominates over competing reactions (such as coupling, see figure 3). The monoimine formed reacts further to give p-benzoquinone, and it is believed that humic acids are the eventual products. Reactions similar to these also occur with substituted p-phenylenediamines to give additional reaction products, and in some cases they are quite complex.

Dialkyl diimines apparently hydrolyze rapidly to aliphatic amines and p-benzoquinone. As in the previous example, the reaction rate is influenced

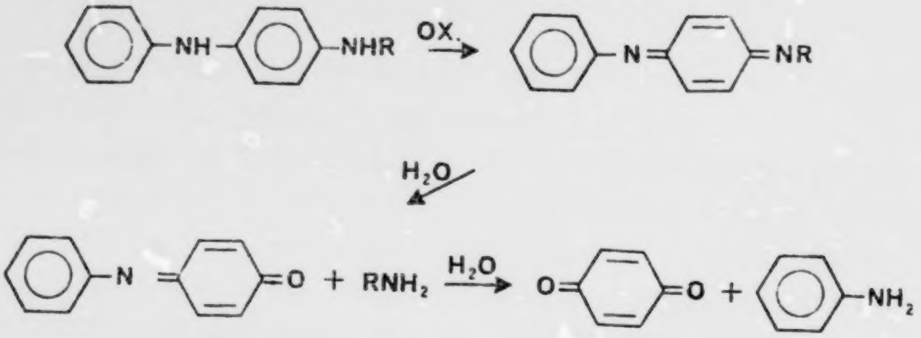

Figure 4. Proposed mechanism for the oxidation and hydrolysis of an alkyl-aryl substituted p-phenylenediamine.

by pH, temperature, and concentration. The hydrolysis rate of the quinonediimine increases as its concentration in water decreases. Alkyl substitution at the amine group also appears to accelerate the hydrolysis reaction (ref. 7).

The fate of the mixed alkyl-aryl p-phenylenediamines is not as clearly defined. To date, no studies have been uncovered which describe the products formed from the aryl substituent subsequent to oxidation and hydrolysis. Oxidation of the mixed substituted p-phenylenediamines could possibly follow the scheme presented in figure 4.

Hydrolysis undoubtably occurs at the alkyl-substituted imino group (refs. 8,9). In view of the apparent stability of the diaryl substituted diimines, however, it is questionable how rapidly they undergo uncatalyzed hydrolysis. While the hydrolysis of an alkyl group is rapid, hydrolysis of the phenylimine linkage is apparently a good deal slower. Hydrolysis of the phenyl benzoquinone imine would be expected to produce aniline and p-benzoquinone. It is also possible that phenyl benzoquinone imine might react by self-condensation, addition reactions, and/or oxidative reactions to yield other reaction products. In the absence of other reactants, however, hydrolysis would be expected to predominate in dilute aqueous solutions. Under these conditions, the mixed p-phenylenediamines would most likely form alkyl amines, p-benzoquinone, and aniline as the principal alteration products.

Only relatively small tonnages of diaryl-p-phenylenediamines are used as antiozonants and antioxidants in tires. Because of their low water solubility, they would be expected to leach from tires to a lesser extent than either the dialkyl or the mixed p-phenylenediamines. It would therefore be expected that smaller total quantities of these materials would eventually enter the environment. These factors, however, compelling as they seem, could possibly be counterbalanced by other considerations. For example, both the diaryl amine and the corresponding diimine are relatively stable. Because of their low water solubility and probable environmental stability, they would be more likely to accumulate in fat. Diaryl p-phenylenediamines can couple even in very dilute solution to give complex reaction products. If hydrolysis proceeds at all, it probably occurs at a very slow rate. However, it must be admitted that very little is actually known concerning the environmental fate of the diaryl products.

In summary, on the basis of current information, it would appear that the bulk of the substituted p-phenylenediamines are retained in rubber tires, and only small amounts of the original antiozonant or antioxidant are leached by water to the environment. This free amine may subsequently be altered by oxidation and hydrolysis, and its principal alteration products are thought to be anilines, aliphatic amines, and p-benzoquinone. As these are labile compounds, they would be expected to undergo additional transformations in the environment through biodegradation, photodecomposition, bacterial action, and oxidation.

It is apparent that some important gaps exist in the available information. For example, the exact nature of the alteration products formed in the tire is not known, and under environmental conditions, it is not known which products are most likely to form from the degradation of the phenyl benzoquinone imines and the diaryl p-phenylenediamines. Several reaction pathways are likely, and one can certainly speculate on which is most probable. At this time, however, the data necessary to justify any firm conclusions are not available. The investigation of these compounds will be continued in an attempt to determine their environmental fate and the likelihood of their entry into the human food chain.

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DISCUSSION

MR. ROBERT J. DOWLING (Uniroyal Chemical Co., Naugatuck, Conn.): Have you at this point found any indication of any TPA or TPA-related compounds in food, and if so, is there any rationale to support the feeling that, if you did find trace amounts, there would be any hazard?

DR. HOLLIFIELD: In answer to your first question our work has not progressed to the stage to where we have analyzed foods. Therefore, I think it would be premature to respond to the second question at this time.

MRS. JAMES H. ANGEL (Citizens for Land and Water Use, Cleveland Metropolitan Area, Cleveland, Ohio): In Lake Erie in Ohio, fish were contaminated. Some fish were confiscated by the U. S. Government and impounded until the case was heard. They were confiscated because of mercury content. They were kept frozen, and then the fish were released and sold in Michigan. I would like to know how the Food and Drug Administration allowed that to happen.

DR. HOLLIFIELD: The answer to that is--I don't know. I am sure that if the fish were confiscated, there was some question as to the mercury level in the fish, and that it might have to be determined if the fish met guidelines that are established by FDA. Presumably, since the fish were released, they met those guidelines.

DR. DAVID C. DAY (Roy F. Weston, Inc., Houston, Texas): In view of the fact that these amines have not been found in food, that the potential has not been identified, why is there interest in them? I might sound facetious, but I missed the point on them.

DR. HOLLIFIELD: These compounds are of interest because they are, first of all, aromatic amines, which are under investigation as a part of the overall project to determine whether or not such compounds are getting into foods. They are relatively high-production volume amines. Not a great deal is known about their environmental fate, and it is our job in the Chemical Division of Technology to determine whether or not these materials do get into foods. If they get into foods, then we determine at what levels they are found. Then, this information is carried forward to determine in a broader survey what type food they get into and at what levels, and where these problems are most likely to occur. In fact, we try to define the problem as completely as possible. Perhaps I did not stress the point enough that this is a part of a program that is in a quite early stage of development. We have not yet begun conducting food surveys to find out whether or not these materials are there. We have, primarily, been gathering preliminary information to determine the probability of whether or not they might get into foods.

CHAIRMAN MCCORMICK: Dr. Hollifield, would you pursue that just a little further. I am curious why the Food and Drug Administration is specifically interested in aromatic amines.

DR. HOLLIFIELD: This goes back to the fact that a number of aromatic amines have been identified as carcinogens. A number of them also have been identified as being toxic either acutely or chronically. Because we are attempting to try to define the problems before they exist, we felt it was wise to look at aromatic amines in general to determine whether or not they get into foods and, if they do, to learn if they pose a real threat to the consumer. Our first interest is the welfare of the consumer. In attempting to define problems before they arise, you have to take shots at potential problem areas and this looked like a likely target.

MR. DOWLING: This is not a question; it is just a comment or statement. Dr. Hollifield must know that under the current Food Act as law, many of the compounds referred to have been reviewed rather carefully by FDA and have been judged safe to be used in products that do come in contact with food; therefore, we strongly suggest that there are not any real hazards.

DR. HOLLIFIELD: A number of materials previously recognized as safe are in process of review. We have become aware, very acutely aware, in the last few years of a number of compounds which have been used in industry for many years without problems being recognized. For example, mercury was used in chlor-alkali plants without any thought of any real problem existing. In the last few years, we found that the elemental mercury has been discharged from a number of these plants and modified by bacterial action to such compounds as methyl mercury. Our review of certain materials is an attempt to try to stop these problems before they really become very serious. That is why we are very interested in aromatic amines in general.

HALOGENATED HYDROCARBONS IN RUBBER PROCESSING

Walter D. Harris, Ph.D.*

Abstract

The rubber processing industry involves not only companies that fabricate rubber but also those making textiles, chemicals, and plastics. Some also fabricate plastics, a wide variety of mixtures and composites of fabrics, plastics, and rubbers. Some of the large companies are in unrelated businesses such as metal fabrication. Thus, almost any chemical may be used in a company generally thought of as a rubber processer.

This paper makes only brief mention of vinyl chloride and deals with the halogenated polymers (used alone or in mixture with conventional rubbers to impart improved properties), halogenated solvents, plasticizers, and flame retardants.

In general, the typical use of the above materials does not present a difficult environmental problem. Local plants may have specific problems which will need individual attention. Some of these materials are likely to be incinerated either as process wastes or after their normal life. The hydrogen halide gases produced may occasionally present a corrosion problem; however, in the community at large, this should not be a serious problem.

This conference is concerned primarily with chemicals used in rubber processing as opposed to those used in making synthetic rubber on one hand and those used in plastics fabrication on the other. If we then restrict ourselves to halogenated hydrocarbons used in rubber processing, there is not a great deal to talk about. Therefore, I will take the liberty of broadening the subject slightly.

American industry seldom confines itself to one product line. Thus, UNIROYAL started out as a rubber fabricating company under the name U.S.

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*Industrial Toxicologist, UNIROYAL, Inc., Oxford Management and Research Center, Middlebury, Connecticut 06749.

Rubber Company. Then, it broadened into growing and importing natural rubber, and it began making chemicals and fabrics needed in fabrication of the end products. In World War II, its Chemical Division began to make synthetic rubbers, plastics, and even agricultural chemicals. Its fabricating plants make products from virtually all types of rubbers, from natural to polyurethane, as well as from plastics; and a wide variety of processes and equipment is used. Other companies are similarly diversified. For this reason, it is unwise to say that a given material is not used in the industry. Almost any chemical may be used by some rubber company for a nonrubber use; and many are used in some very small volume specialty items.

The above fact can be illustrated by citing vinyl chloride, one of the largest volume plastic monomers. B. F. Goodrich is one of the largest manufacturers of both the monomer and the polymer PVC. Goodyear, Firestone, UNIROYAL, and General are all involved in making monomer and/or polymer PVC, and many of the rubber companies of all sizes fabricate it into a wide variety of consumer products. I will not dwell on the toxicity of vinyl chloride since EPA is already well acquainted with it and has made a study of the environmental problems caused by all segments of the industry (ref. 1).

Polymers

The largest volume rubbers are hydrocarbons. All halogenated rubbers fall into the broad category of halogenated hydrocarbons. Many manufacturers both here and abroad are experimenting with various fluorinated, chlorinated, and brominated rubbers to improve the performance of rubber for specialized applications. Decreased permeability of various gases; resistance to ozone, solvents, heat, and light; and improved processibility are the desired properties. Typically, applications are of relatively small volume and scattered so that the use of these rubbers in any one plant at present tends to be very small. Other than PVC, the combined volume of these specialty halogenated polymeric hydrocarbons make up roughly 5 percent of the total rubber used in the United States. (This of course leaves the typically plastic uses of PVC out of consideration. The total volume of PVC used in the United

States is nearly as large as the total volume of rubber used.) Typical of these materials, somewhat in the order of volume produced, are the following:

- Chloroprene rubber--cements, adhesives, and specialty rubbers where resistance to chemicals, sunlight, ozone, and solvents is of special importance;
- Polyvinyl chloride--as a modifier for "nitrile" rubber to improve processing and to impart ozone resistance;
- Chlorinated and brominated butyl rubbers;
- Chlorinated polyethylene;
- Chlorinated natural rubber;
- Fluorinated rubbers;
- Liquid bromine terminated polybutadiene.

None of these halogenated polymers are toxic per se due to their low solubility in cellular fluids. As with any other material, they may constitute a solid waste disposal problem for plants using them. Their biological degradation is slow and they will slowly release chloride, bromide, or fluoride ions. It seems unlikely that this would cause a serious water pollution problem. Incineration of either the raw polymer or fabricated products will lead to release of HF, HCl, or HBr. The fluorinated rubbers, such as the Viton® rubber, are used in small volume at present. HCl and HBr released from incinerators that burn substantial amounts of the chlorinated or brominated polymers are more likely to cause corrosion problems in the incinerator or its immediate environs than to create a health problem or agricultural damage. The uses are so specialized that these polymers would normally make up an almost insignificant part of the feedstock for any given incinerator, other than a waste incinerator operated by the manufacturer of the halogenated polymer itself.

The chloride ion is common in nature, and the body has a great deal of buffering capacity. HCl and HBr are irritants at concentrations far higher than would normally result from incineration of the above polymers. Chronic effects are unlikely because both the chloride and bromide ion are readily eliminated in the urine. Darmer et al. (ref. 2) have recently studied acute effects of high concentrations of HCl both as the gas and as an acid aerosol. Both forms produce the same effect.

While these are irritating and toxic at high concentrations, there is nothing to suggest toxicity at low concentrations such as might be encountered in community air from burning solid wastes produced by a fabricating plant or burning the wornout products made from these polymers.

Solvents

Solvents have many uses in a rubber plant, some not peculiar to the rubber industry. A major use is the dissolving of rubber to make rubber cements. Because of the nature of the large volume rubbers, chlorinated hydrocarbons are not very good solvents. They are also relatively expensive. Gasoline and naphtha or aliphatic hydrocarbons such as hexane or heptane are more commonly used. Toluene and xylene are also used. Patty (ref. 3) gives an authoritative though somewhat dated discussion of toxicity of a wide variety of halogenated hydrocarbons.

Fluorocarbons

As in any industry, certain of the fluorocarbons are used as refrigerants. To a minor extent, they may be used as propellants but this use is minor in the rubber processing industry compared with the aggregate use in propellants for aerosols in the home. The biggest single use is as blowing agents in polyurethane foams. The main ones are:

- Trichlorofluoromethane--both rigid and flexible foams;
- Dichlorodifluoromethane--blowing agent for flexible foams;
- Trichlorotrifluororethane--blowing agent for flexible foams.

It can be assumed that all of these ultimately are discharged to the air. They are not toxic per se.

Methylene Chloride

While not a preferred solvent for uncured conventional rubbers, methylene chloride is used commonly in the polyurethane foam industry to flush spray nozzles between runs. It is a very volatile solvent of low toxicity and moderate cost, so it is used in a variety of specialized applications. Its use in paint removers and as a solvent for certain plastics is much larger than its use in rubber processing. Of course, paint removers are used in maintenance operations as in any industry.

Chloroform and Carbon Tetrachloride

Because of toxicity, these chemicals have been virtually eliminated from the rubber fabricating industry. They are used in laboratories for specific operations, but this use is very small.

1,1-Dichlorethylene or Vinylidene Chloride

This is used as an intermediate in plastics.

1,2-Dichloroethane or Ethylene Dichloride

This is used as an intermediate chemical for vinyl chloride and certain other commercial chemical processes. It is also used as a solvent in some chemical operations but not commonly in the rubber industry per se.

1,1,1-Trichloroethane

This is used as a "safety" solvent. The name is a misnomer since its safety is relative. It is much less toxic than carbon tetrachloride and is much less of a fire hazard than many of the other solvents commonly used. It is not typically a good rubber solvent for making cements. It is used more for cleaning surfaces.

While it is much less toxic than carbon tetrachloride, it is very volatile. At high concentrations, it is a liver poison but is not toxic at concentrations conceivable in the air surrounding a rubber fabricating plant.

Trichloroethylene

Trichloroethylene is used for metal degreasing and as a dry cleaning solvent. It is not commonly used as a rubber solvent. Use in the rubber industry is, therefore, quite limited in volume.

The properties commonly ascribed to the chlorinated solvents--anesthesia, liver damage, skin irritation--are not likely to be problems in the low concentrations to be found in the air around a fabricating plant. In some instances, concentrations in water could be toxic to aquatic life, especially in the event of a spill.

Medium Molecular Weight Halogenated Hydrocarbons

A number of materials are being studied as flameproofing agents, alone or in combination with such materials as antimony trioxide and phosphates. Such uses are largely confined to the plastic side of the business, especially in foams. The chlorinated diphenyls are no longer sold for any but closed system use. Materials such as hexabromobenzene may be so stable that they will distill out of incinerators unchanged. Unless they are toxic in the environment, this might not cause harm.

It would be unwise, in this writer's opinion, to force industry to move too rapidly in the flameproofing field until the materials can be adequately studied. In view of the environmental concerns caused by the widespread use of the insecticides DDT, chlordane, dieldrin, aldrin, endrin, and related materials, there is a tendency to suspect all the highly halogenated hydrocarbons of similar molecular weight. It should be recognized that these are specific, biologically active chemcials developed specifically to kill insects. Each was the end product of many man-years of research to find highly toxic chemicals with long residual activity. Many of the flameproofing compounds under study may be equally stable in the environment but, if not active biologically, may do no harm. Sand is very stable but is toxic only when airborne in a particular narrow particle size range. Unlike the insecticides, these flameproofing compounds would not be sprayed over the landscape. They should be watched, but there is no need for a panic approach.

In considering halogenated hydrocarbons or any other chemicals, it really comes down to the fact that every plant is a living, changing entity. The planning should start back in the laboratory and carry right on through to the daily operation with full understanding and backing of top management. There is no way that government can force industry to "be good" without forcing them out of business. There should be a cooperative effort backed by good laws enforced wisely as a last resort. The ancient Hebrew prophets longed for the day when men would want to live in harmony with God's laws. We've got a way to go but I am hopeful that this conference is a small step in that upward climb.

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DISCUSSION

MS. JOAN COOK (Citizens for Clean Air and Water, Cleveland Area, Cleveland, Ohio): Cleveland doctors were using fluorocarbons for anesthetics. I think that concerning many of the chemicals you have mentioned we need to emphasize that they are absorbable through the lungs, that they do affect the senses and nervous systems, and that some of them affect the circulatory system. From the use of fluorocarbons it was found that there was liver pickup, which the British doctors did not find in their patients. So the British doctors came over to this country with their product and then got the liver pickup. So the question came up, and this has been debated in the medical profession, as to whether or not this liver damage in patients brought in for surgery occurs from daily exposure to some of these hydrogenated fluorocarbons before they ever received a general anesthetic.

DR. HARRIS: It may be true that some of the fluorocarbons have a degree of toxicity if there is sufficient exposure. The thing I was trying to point out about this particular industry under discussion, is that there is really very little exposure generally. Definitely, halogenated hydrocarbons in many cases are liver poisons, if you get enough of them.

MR. J.S. PHILLIP WILSON (Local 17 of United Rubber Workers, The B. F. Goodrich Company, Akron, Ohio): I was wondering, concerning the process of curing GRS in the vulcanization process, if you can give me any idea of the toxicants that are in the fumes in vulcanizing the rubber.

DR. HARRIS: Well, I think that is the subject of another paper. Are you talking about halogenated hydrocarbons particularly?

MR. WILSON: Well, I was wondering if they are released in the process.

DR. HARRIS: Do you mean, would the halogenated hydrocarbons be released? Primarily in tires?

MR. WILSON: Yes, GRS?

DR. HARRIS: I cannot really think of any appreciable use, can you, Mr. McCormick?

CHAIRMAN McCORMICK: I think the gentleman is asking what you know about the composition of and the effluents from the curing of GRS--is that right?

MR. WILSON: That is right.

DR. HARRIS: I am not going to attempt to answer it deliberately because I think this is perhaps going to be discussed in one of the later papers. I would prefer therefore, that you hold it, perhaps, and we can come back to it a little later on.

DR. STEPHEN M. RAPPAPORT (Los Alamos Scientific Laboratory, Los Alamos, New Mexico): Dr. Harris alluded briefly to the vinyl chloride situation. Of course, this is a chlorinated hydrocarbon which is highly used in the rubber industry. Recently, vinyl chloride got a great deal of notoriety, as have the other chlorinated monomers of chloroprene and vinylidine chloride, both which have recently been implicated as carcinogens. I think their inclusion is highly debatable at this point. I just wondered if Dr. Harris would comment briefly as to whether or not this is setting a type of trend concerning monomer chlorinated compounds that might in the future actually show up as a severe class of carcinogenic compounds.

DR. HARRIS: Of course I think it is starting a trend, since it alerts everyone that there is a possible problem they had not realized, and since it is causing everyone to go back to the drawing board and look hard at the materials they are using, whether they are chlorinated or not. I am sure there will be a tendency to look at other chlorinated materials such as chloroprene, to see if indeed they are bad actors in one way or another.

We have to watch the rubber called chloroprene specifically, and the monomer from which it is made. This is really the thing that is under question--in a work that was published in Russia and made available in Russian.

I am in the process of determining what our use of these is in our plants. We do indeed use a lot of chloroprene rubber and some latex. Latex would more likely be a problem; there is much higher exposure to chloroprene vapor because there is more chloroprene monomer in the latex.

As far as the rubber is concerned, I would have to conclude at this point that it is extremely unlikely that there is any problem there.

In the case of the latex, it is theoretically possible that there could be significant exposure judging from our experience sampling for other vapors. I do not see any data that really gets me terribly excited, but we are going to have to look at it carefully. Now let me see, you asked about--what was the other one you asked?

DR. RAPPAPORT: Vinylidene chloride?

DR. HARRIS: Vinylidene chloride, of course, is under study. We have done a little work and it is a little difficult to find out what it is. It is not at all, I would think, conclusive at this point, but again it is being studied. I think the various industries involved, in this case, the chemical industry, are being very responsible and not taking chances. I think the big danger here is that people jump to conclusions because there is some chemical relation--because it has got chlorine or chloro or vinyl in the name, that it is automatically like vinyl chloride. This just does not follow at all. When you know what really happens in the case of vinyl chloride and really understand the metabolism in the human organism, then you will probably understand very well why some of these materials are not problems.

MR. BOBBY D. LaGRONE (U.S. Rubber Reclaiming Co., Inc., Vicksburg, Miss.): At what temperature would you expect to get a breakdown of chlorinated and brominated rubbers to the corresponding hydrochloric or hydrobromic acid you spoke of?

DR. HARRIS: I was talking in terms of an incinerator temperature. I think with organics--when you get up to 600 to 800°F--you are going to get a lot of breakdown. I am just not sure where that point would be, but my feeling is that it would be considerably higher than the normal processing temperature. An incinerator is designed to take the organic material apart.

HEALTH STUDIES RELATING TO CARBON BLACK*

Carl A. Nau, M.D.[†]

Abstract

Furnace carbon black, a product of the incomplete combustion of gas, oil, and oil sludges, or a mixture of these, has adsorbed polycyclic aromatic components, which can be desorbed by various solvents, of which benzene is the best. Some components of this extractive are admittedly carcinogenic.

Furnace carbon black with its adsorbed polycyclic aromatic may be ingested, injected subcutaneously, or applied to the skin of mice without detectable changes from the normal. The desorbed components when ingested, injeected subcutaneously, or applied to the skin of mice will produce tumors.

Inhalation of a furnace carbon black by mice or rhesus monkeys leads to the accumulation of carbon black within the lung without damage to pulmonary function, and it also leads to electrocardiographic changes indicative of right atrial, septal, and right ventricular hypertrophy. Increase in heart weight may also be noted. No tumor formation was noted in the lungs or elsewhere.

Epidemiologic investigation of men working in carbon black for 17 years reveals that the observed death rate from cancer as well as the morbidity rate is no higher than for other comparable populations.

Studies on animals and man, sponsored by the carbon black producers, have been conducted since 1949.

Historical

The first carbon black plant using natural gas as the raw product was built in New Cumberland, West Virginia, in 1872. West Virginia remained the chief producer until 1920, when owing to rising costs of

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*The studies used as a basis for this paper were funded by carbon black producers and conducted at the University of Texas at Galveston and University of Oklahoma School of Medicine, Oklahoma City, Oklahoma.

[†] Consulting Professor, Health Sciences Center, School of Medicine, Texas Tech University, Lubbock, Texas 79409.

natural gas in West Virginia and Pennsylvania, Louisiana became the leading producer. It held this distinction until 1929, when Texas became the number one producer. Among the other States now producing substantial amounts are New Mexico, Arkansas, Oklahoma, and Kansas.

Each year the amount produced has increased. The 1973 production of furnace carbon black in the United States was somewhere near 3,174,000,000 pounds.

Carbon black, the finely divided carbon resulting from the incomplete combustion of gas, oil, and oil sludges--or mixtures of these materials--is becoming increasingly more important because of its increased usage, especially in the rubber industry.

While all carbon blacks are the product of incomplete combustion of carbonaceous fuels, there are three major types resulting from three different processes of manufacture. These are:

1. The impingement or channel process, in which fine-particle (highly agglomerated) blacks are made entirely from gas; the average particle diameter is 50-300Å;
2. The furnace process, using either gas or oil or a mixture of the two, in which, by varying the operating conditions, blacks of graded sphere diameter can be produced; the average diameter is 300-800Å.
3. The thermal process in which hydrocarbon gases are used to produce coarse blacks, which have very little tendency to agglomerate; the average particle diameter is 1,200-5,000Å.

From time to time inquiries have been made concerning the possible health effects of contact with carbon black of the various types. Because not a great deal of investigative work had been done--judging from the scarcity of publications up to 1949--the carbon black producers, as a cooperative effort, initiated studies in 1949 to determine factual information on the possible health effects of contact with the various types of carbon black. These studies are still underway (refs. 1-5). They involve contact with the various type blacks by,

1. Ingestion;
2. Skin contact--surface and subcutaneous;
3. Inhalation;

4. The separation, identification, and quantification of the various polycyclic aromatics adsorbed on carbon black;
5. An epidemiological study of workers in carbon black whose work and health records were adequate and available (refs. 6,7).

Because this conference is concerned with the environmental aspects of chemical usage in rubber-processing operations, my remarks will be focused on the use of carbon blacks made by the furnace process, which, according to my information, is the type of carbon black having a major usage in the tire-processing industry.

Carbon black has characteristics that distinguish it from bone black, charcoal, and chimney soot. It is essentially carbon combined with hydrogen and oxygen. The hydrogen is residual hydrogen from the hydrocarbon raw material and is more or less evenly distributed. It is thought to be bonded to the carbon atom by true valence bonds leading to an "unsaturated" state. The oxygen is chemisorbed on the carbon surface. The amount of oxygen present has an effect of the properties of the black--the more chemisorbed oxygen, the greater is the hydrophilic property of the black and the more acidic the water sludge of this black becomes. The properties imparted by the chemisorbed oxygen are very important to the rubber industry. The chemisorbed oxygen and hydrogen present on the carbon black are termed "volatile matter" and may be determined by heating most of the blacks to 1,200°C.

The ash content of furnace black varies in kind and amount with the chemicals present in the quenching water and may be as high as 1 percent.

Early in our studies it became evident that the furnace type carbon blacks had an adsorbed component that could be removed (in whole or in part) by continuous extraction (48 hours), especially with hot benzene using a soxhlet extractor (ref. 1). Other solvents were not as effective as benzene. The quantities of material extracted by 48 hours of continuous extraction were determined. This extractable material was studied extensively--using methods of separation involving chromatographic techniques (column, plate, paper, gas, etc.) making every effort including repeated separations to get pure compounds with identifiable U-V spectra.

The following polycyclic aromatic hydrocarbons adsorbed on an SRF carbon black chosen as an example of a furnace carbon black made from an oil-enriched gas and having the largest particle size and the highest benzene extract were identified and quantitated (ref. 8). The sample analyzed was produced in 1964 and was not then, nor is it now, a typical furnace carbon black.

1. Anthracene
2. Phenanthrene
3. Fluoranthene
4. Pyrene
5. Benzo (mno) Fluoranthrene
6. Chrysene
7. 1,2-Benzanthracene
8. 9,10-Dimethyl - 1,2-Benzanthracene
9. 1,2-Benzopyrene
10. 3,4-Benzopyrene
11. Perylene
12. o-Phenylene pyrene
13. 1,12-Benzoperylene
14. Anathrene
15. Coronene

Of these, 1,2-benzanthracene; 9,10-dimethyl - 1,2-benzanthracene; 3,4-benzopyrene; and o-phenylene pyrene are known carcinogens.

Other compounds were separated from the total benzene extract, U-V spectra were obtained, but these were not identified due to the lack of suitable standards. We had the following 28 standards on which we obtained and recorded U-V absorptions spectra is isooctane and in hexadecane.

We also had literature U-V absorption spectral data as recorded by Clar (ref. 9) and Sawicki et al. (ref. 10).

It was our opinion that we should concentrate on identifying and quantifying 3,4 benzopyrene and use this as an indication of our potential problem. The following studies were done:

1. "Whole furnace carbon black--as a 10 percent in Purina Dog Chow was fed to C_3H and CFW male mice for 72 weeks (ref. 1). Gross and postmortem examinations revealed no changes from the normal as compared to control mice;
2. The total benzene extract of a furnace black was incorporated in Purina Dog Chow and fed to C_3H and CFW mice. A significant number of malignant tumors was found in the G-I tract of the mice fed (ref. 1);

3. A known carcinogen (methylcholanthrene) mixed with Purina Dog Chow was fed to C_3H and CFW mice. A significant number of malignant tumors was found in the G-I tract of the mice fed (ref. 1);

Table 1. Polycyclic aromatic hydrocarbons standards and their sources

Hydrocarbon	Sources
Pyrene	Eastman Organic Chemicals
Chrysene	Eastman Organic Chemicals
Fluoranthene	Eastman Organic Chemicals
3-Methyl cholanthrene	Eastman Organic Chemicals
1,2-Benzanthracene	Eastman Organic Chemicals
Anthanthrene	K & K Laboratories, Inc.
1-Methyl pyrene	K & K Laboratories, Inc.
9,10-Benzophenanthrene	K & K Laboratories, Inc.
1,2,3,4-Dibenzpyrene	K & K Laboratories, Inc.
3,4,8,9-Dibenzypyrene	K & K Laboratories, Inc.
3,4,1,10-Dibenzpyrene	K & K Laboratories, Inc.
1,2,3,4-Dibenzanthracene	K & K Laboratories, Inc.
3,4,5,6-Dibenzophenanthrene	K & K Laboratories, Inc.
1,2-Benzopyrene	Aldrich Chemical Co., Inc.
Perylene	Aldrich Chemical Co., Inc.
Phenanthrene	Aldrich Chemical Co., Inc.
o-Phenylene pyrene	Aldrich Chemical Co., Inc.
1,12-Benzoperylene	Aldrich Chemical Co., Inc.
9,10-Dimethyl anthracene	Aldrich Chemical Co., Inc.
1,2,5,6-Dibenzanthracene	California Corp. for Biochemical Research
9,10-Dimethyl-1,2-Benzanthracene	California Corp. for Biochemical Research
5,10-Dimethyl-3,4,8,9-Dibenzpyrene	California Corp. for Biochemical Research
Coronene	Fluka AG, Buchs, SG, Switzerland
3,4-Benzopyrene	J. T. Baker Chemical Co.
Anthracene	Chemical Service Media
Naphthacene	City Chemical Corporation
1,2-Benzanthracene (tetraphene)	Nutritional Biochemicals Corp.

4. A known carcinogen (methylcholanthrene) adsorved chromatographically (with heat) on a furnace carbon black that had previously been extracted with hot benzene was fed to C_3H and CFW mice for prolonged periods. None of the fed mice developed malignancies. This result suggests the adsorptive power of carbon black and the effective inactivation of a known carcinogen (ref. 1);
5. Tests were designed to determine whether gastric juice, intestinal juice, or human blood plasma would desorb any of the carcinogenic polycyclic aromatics adsorbed on a furnace carbon black (ref. 3). The carbon black was suspended in these various potential eluents for 7 days using benzene extraction of the eluent and subsequent examination of the benzene by scanning with a U-V spectrophotometer. It was determined that under these conditions no carcinogen was desorbed;
6. It was also found that subcutaneous or intraperitoneal injection of the "whole" furnace carbon black in mice in significant quantities led to no detectable changes from the normal. Injection of the benzene extract produced tumors (ref. 3);
7. Tests were also designed to determine if gastric juice, intestinal juice, or human blood plasma would desorb any of the carcinogenic polycyclic hydrocarbons adsorbed on a furnace carbon black incorporated in a typical rubber formation (10 or 20 percent) obtained from a commercial fabricator. It was determined that the eluents used did not elute any significant amounts of polycyclic aromatics from the rubber formulations (ref. 3).

Skin Contact Studies (ref. 2)

Mice, rabbits, and monkeys were painted with a 20-percent suspension of a furnace carbon black in water (using 1 percent aqueous carboxymethycellulose as the emulsifying agent), cotton seed oil, or mineral oil--three times a week for 1 year. No changes from the normal were detected.

When the benzene polycyclic adsorbed component of this same carbon black was painted on these same species, a significant number of the painted animals developed skin malignancies.

These tests indicate that carbon black adsorbs the polycyclic aromatics so firmly that either they are not released at all or are released so slowly that they are ineffective as carcinogens.

Inhalation Studies (ref. 4)

These were more extensive and used various furnace carbon blacks. Mice, guinea pigs, and rhesus monkeys were used as test animals. To accomplish our purpose we designed an air-tight dust chamber 6x8x10 feet in size with an entrance door of 2x6 feet. We used a dust concentration of 1.6 mg per cubic meter. This concentration was higher than one would find under the usual working conditions and was selected after tests at the sacking department. Temperature and humidity were approximately 76°F and 55 percent. Our dust feed apparatus was designed to maintain a fixed and continuous, relatively uniform concentration. Our animals were exposed 7 hours per day 5 days per week. The monkeys were exposed for as long as 13,000 hours and the mice for their life span. Food and water was available at all times. Relevant controls were carried out for all tests. All animals were subjected to gross and microscopic tissue and organ studies.

It should be pointed out that not all of the particles inhaled remain in the lung. Some are too large to penetrate far into the tubular system, and smaller ones penetrate deeply but may also be exhaled.

The pulmonary system has fantastic capabilities of self-cleansing, made possible by the secretory powers of the tubular lining cells and the coordinated, sychronized movement of the cilia projecting into the tubular system. Unless this capability is exceeded, very few particulates will be detected by microscopic examination. Assuming, however, that the capability for self-cleansing may be exceeded at times for one reason or another, particles may be found in lesser or greater amount--free or engulfed in scavenger cells (macrophages).

The furnace black inhaled by our test mice entered the alveoli (terminal parts of the lung, where the gaseous exchange takes place) readily and could be demonstrated as free-lying particles, or sometimes aggregates of the particulates were found in macrophages (scavenger cells). This intra-alveolar pigmentation was uniformly distributed (irrespective of particle size) throughout the pulmonary parenchyma, and its intensity was a direct correlation with the duration of exposure. The maximum intensity was reached at 2,000 hours of exposure.

Little or no carbon black was found in the alveoli of our exposed rhesus monkeys, irrespective of the length of the exposure; in only rare instances were pigmented macrophages observed.

Carbon black may be found within the wall of the alveolus--having penetrated into the interstices. The alveolar lining cells contained minimal or virtually no pigment. The pigment was, however, found interstitially either as a free particulate or within the macrophages. The interstitial location became more predominant than the alveolar within 1,000 to 2,000 hours of exposure. Within the alveolar interstices, the pigment became more compacted in a dense manner much more prominently than could be demonstrated in the intra-alveolar state.

In mice, the carbon black was diffusely and finely distributed. In contrast, the monkey lungs primarily presented the pattern of focal nodular pigmentation diffusely distributed throughout the lungs in such a manner as to give the gross appearance of uniform total blackness; however, large areas of alveoli demonstrating no pigmentation were found interposed between the areas of nodularity.

In most instances, the physical presence of the carbon black alone accounted for a thickening of the alveolar walls. Some alveolar wall thickening due to cellular proliferation was encountered. In a few animals, there was proliferation of the interstitial cells, and only rarely did this change lead to a minimal and variable fibrosis. No common factors could be determined to predict which animals would or would not develop this fibrosis, nor did it progress as exposure continued.

With progression, the carbon black was observed characteristically in two locations, peribronchial and perivascular. This distribution was manifested as prominent aggregates or nodules of pigment and was observed especially in the monkey lungs. These heavy deposits of carbon black were present both in the free state and within macrophages and were within perivascular and peribronchial soft tissue. The uniform peribronchial carbon black deposition served to intensify the bronchial passages radiographically. The subpleural lymphatics were also prominently distended with carbon black. The bronchopulmonary hilar lymph nodes displayed varying degrees of pigmentation. No fibrosis was observed within the lymph nodes.

Emphysema was encountered irregularly, but certainly it did occur in varying degrees, usually focal and usually minimal. The significance of the emphysema in both mice and monkeys is difficult to determine, because it has been observed also in some of the control animals. This emphysema tends to be centrilobular in type and, therefore, probably due to the physical presence of the carbonaceous material, or it may be a sequel to an old inflammatory reaction.

Microscopically, the liver, spleen, and kidneys of the exposed animals demonstrated the presence of some carbonaceous material but no significant changes from the normal.

We did not do any pulmonary-function studies on the monkeys exposed to the furnace carbon black but did do both antemortem and postmortem function studies on monkeys exposed to carbon black made by the thermal process (ref. 11). No changes from the normal were detected. The microscopic pictures of both groups (furnace or thermal) were identical.

Chest X-Rays of the Exposed Monkeys (ref. 4)

No changes on the chest X-rays were noted until 250 hours of exposure were reached, at which time slight changes were noted. After 1,000 hours of exposure, the changes noted were quite definite and increasing as the exposure continued. The changes consist of "blotchy" irregular areas of infiltration scattered throughout the lower portion of both lungs. The infiltrations predominantly occupy the lower portions, although there appears to be some infiltration in the upper portions of the lungs. The degree or extent of the infiltration appears to be about equal in all of the monkeys with equal exposure and increases with increasing exposure. In all of the monkeys exposed for 1,500 hours or more, there are definite, well-marked, extensive changes in the lungs characterized by definite areas of opacity. In those monkeys exposed for 2,000 hours we found no striking changes compared to those exposed for 1,500 hours.

Electrocardiographic Changes (ref. 4)

Monkeys inhaling the furnace carbon black showed electrocardiographic changes resulting from atrial and right ventricular strain and were noted first after 2,500 hours of exposures. After 10,000 hours of exposure the changes were quite marked.

After 1,000 hours of exposure (in mice) there is a slight increase in the ratio of heart weight to body weight.

When we studied the possible effect of the inhalation by monkeys of a thermal-type carbon black we found a resulting right ventricular, septal, and, to a lesser degree, left ventricular hypertrophy.

In a comparison of the ratio of lung weight to body weight--using mice exposed to a furnace black and comparing them to control mice--an increase of threefold to fourfold in the exposed mice in lung weight was detected (ref. 4). This finding warranted a study of pulmonary ventilation in mice. Using the uptake of carbon monoxide as an indication of the amount of air going through the pulmonary system, we exposed our test and control mice to a known concentration of carbon monoxide for an equal time period. Blood carboxyhemoglobin that was determined in both groups 5, 10, and 20 minutes after the exposure ended showed no significant difference in the two groups. This finding, together with the finding of our pulmonary function studies in our monkeys exposed to a thermal black by inhalation, suggests that there is no impairment in air flow or in diffusion of gases.

An epidemiological study of men who worked for 17 years in plants producing carbon black was conducted (refs. 6,7). The number of workers serving as a basis for this study, their ages, and length of time worked may be questioned as being adequate for conclusions. An extension of this survey involving a larger number of workers is presently being designed.

It was indicated from this study, the observed death rate from cancer among the carbon black workers studies was 0.21 per 1,000 per work year for the 17-year period, 1939-1956. This is low expectancy, as judged by rates observed among other and comparable populations. The morbidity rate also was low--1.0 for 1939-1949 and 1.2 for 1949-1956 (refs. 6,7).

The evidence available from our studies extending over 26 years, coupled with personal observations, leads us to conclude that:

1. The health of the worker exposed to carbon black is not adversely affected by his exposure;
2. In animal feeding, painting or subcutaneously injecting the whole carbon black as produced and used leads to no detectable changes from the normal;
3. Inhalation of the furnace carbon black in high concentrations for prolonged periods (mice and rhesus monkeys) leads to a deposition of the carbon black in the lung with no detectable loss of normal pulmonary function, but with some electrocardiographic and heart-weight changes, suggesting a slight right ventricular, septal and, to a lesser degree, left ventricular hypertrophy;
4. Carbon black made by the furnace process has polycyclic hydrocarbons adsorbed, and these can desorbed in whole or in part by extraction with benzene;
5. The benzene-extractible material has carcinogenic components which, when painted on or injected into mice, produce malignant tumors. A similar result occurs when the extracted material is mixed with Purina Dog Chow and fed to mice.

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CARBON BLACK AND ECOLOGY

Harry J. Collyer*

Abstract

Ecology is the biology dealing with the mutual relationships between organisms and their environment. Carbon black has a unique combination of two properties; it is both the darkest substance and the most finely divided substance. These properties dictate a need for special treatment to insure environmental control. The relationship of carbon black to man and his environment is important. Advancing technology in manufacturing operations has insured compliance with ecological needs. Pelletization and packaging improvements have facilitated shipping, in-plant handling, and use in rubber processing operations. Good housekeeping is essential.

Carbon black safety and health aspects have been documented. Carbon black by OSHA definition is not a hazardous material and is not a toxic substance. The Threshold Limit Value (TLV) relates to good housekeeping. Carbon blacks as used in the rubber industry do not create an explodable atmosphere. Heavy metals, cyanides, phenols, and polychlorinated biphenyls (PCB's) are either absent or present only in trace amounts. Carbon black does not qualify under the OSHA Standard for "carcinogens." An FDA regulation permits carbon black use in rubber articles.

Physiological effects of carbon black on small animals have been studied for over 25 years. Morbidity and mortality studies of carbon black workers indicate no specific health problem. The carbon black industry continues its worker-safety and health studies and its development of products that are ecologically satisfactory.

Ecology may be defined as the biology dealing with the mutual relations between organisms and their environment. Eco derives from the Greek OIKOS, meaning house. Thus we have the study of man in his house, his habitat, the effect of man on his environment, and of his environment on man. The environment is made up of a number of interrelated entities: the atmosphere that Mother Nature provides: the atmosphere after man has lived, worked and played in it; the ground and water below; the surrounding structures; the people around; and the machines and materials man uses for his way of life. Let us consider how one of these materials, carbon black, relates to man and to the environment of rubber processing operations.

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*Technical Service Manager and Product Liability Coordinator, Cabot Corporation, Billerica Technical Center, Concord Road, Billerica, Massachusetts 01821.

Carbon black has a unique combination of two properties, each of which, it will be seen, suggests a need for in-plant control. First, carbon black is the darkest substance known to man. Second, carbon black is the most finely divided commercial substance, several orders of magnitude finer, for example, than the particulates that make up tobacco smoke. It is this fine state of subdivision (along with some other properties) that causes it to be the most important material in the reinforcement of elastomers and plastics. Carbon black handling operations within the rubber factory therefore involve three factors important to ecologists: a product which man feels he must use but a product which likes to be where it shouldn't be and is highly visible when it gets there.

Since our specific interest lies in the environmental aspects of carbon black use in rubber processing operations, we will not dwell too deeply upon the history of carbon black development nor detail methods of manufacture or the parameters governing the choice of a particular grade of black for a specific application. However, to provide proper frames of reference and some definitions, carbon blacks have been broadly classified by the methods of manufacture. Channel blacks are made by impingement of underventilated natural gas flames, thermal blacks by thermal decomposition of natural gas. Gas furnace blacks are made by partial combustion of natural gas in reactors or furnaces and oil furnace blacks by partial combustion of liquid hydrocarbons in reactors or furnaces of more advanced design.

Channel process manufacture began to decline when SBR was developed during World War II and a need for different types of carbon black was recognized. Channel blacks were supplanted first by gas-process furnace blacks and later by oil-process furnace blacks. The channel process is not a "clean" process and in recent years has become esthetically and ecologically unacceptable. As a result of pollution control activities, low yield characteristics, and the increasing cost of natural gas, production of those grades of channel black that were suitable for use in rubber came to an end in the United States last year.

Thermal process blacks remain available, although domestic capacity has been sharply reduced during the past few months. Since the make fuel is natural gas--a commodity of decreasing availability and increasing cost--there is some conjecture as to the continuing availability of thermal blacks at affordable prices. The remaining capacity (about 255 million pounds) represents only about 6 percent of the total domestic carbon black capacity (4.1 billion pounds).

Gas process furnace blacks had a relatively short period of large-volume production before advancing technology introduced liquid hydrocarbon raw materials and the oil furnace process was born. The oil furnace process turned out to be the most important development ever in the carbon black industry. It allowed greater yields per pound of hydrocarbon, greater throughput, greater collection efficiency, and, as knowledge increased, wide flexibility in the types of black produced. Since the make fuel could be easily transported, it opened up plant locations all over the world and, here at home, new plants have been located nearer the larger consumption centers. About 94 percent of the nearly 4 billion pounds of carbon black shipped in the United States goes into rubber products, and it is estimated that about 60 percent of the carbon black shipped to rubber industry customers is used by tire manufacturers. Carbon black's outstanding ability to reinforce elastomers and impart other desirable characteristics make it a commodity essential to our economy and way of life. As such it is appropriate to consider its safety and health aspects and environmental control.

Long before passage of the Occupational Safety and Health Act of 1970 (OSHA) the carbon black industry had established, by all means at its command, that its product was not a hazardous material. A similar conclusion had been reached by the industrial safety and occupational health programs of our customers. It is gratifying to note, therefore, that carbon black does not qualify as a hazardous material by OSHA definition.

Carbon black is technically not on the Toxic Substances List published annually by the National Institute for Occupational Safety and Health (NIOSH).

This requires a brief explanation. In 1971 and prior years carbon black was not listed. In 1972 it appeared on the list on the basis of some detrimental small animal tests reported in a foreign journal. When it was pointed out to NIOSH that the work had been done with lampblack, not carbon black, NIOSH agreed to remove carbon black from 1973 edition, which was done. Carbon black reappears in the 1974 edition but NIOSH has told us this is a printing error, to be corrected in the next edition.

The American Conference of Governmental Industrial Hygienists (ACGIH) assigns and publishes threshold limit values (TLV) for chemical substances in the workroom environment. These are included in the OSHA Standards. The threshold limit value for carbon black is 3.5 mg/m^3 (time-weighted average). This amount creates a very dark cloud and would seldom be experienced. Actually, ACGIH agrees that since carbon black is not a toxic substance, it deserves a TLV of 15 mg/m^3, the level assigned to "nuisance dusts." However, the lower value is being kept for "housekeeping" reasons even though from a health point of view the higher value should be allowed.

The OSHA Standards contain a section extracted from the National Electrical Code, which confirms that carbon black dusts having less than 8 percent volatile matter do not create an explodable atmosphere. Carbon blacks for use in rubber offer no problem; typical volatile contents are about 1 percent. Tests by the Bureau of Mines, by private sector insurance laboratories, and by carbon black supplier laboratories confirm the nonexplosive nature of rubber-grade carbon blacks.

Rubber-grade carbon blacks are extremely difficult to ignite. Ignition in air occurs well above 300°C. When burning, carbon dioxide and carbon monoxide are evolved. While no particular precautions need be taken when handling and storing carbon black, when entering closed storage tanks use of an appropriate respirator or air line is essential to guard against lack of adequate oxygen supply or possible exposure to carbon dioxide and carbon monoxide.

From a reactivity point of view, carbon black is a remarkably inert, stable material.

Carbon blacks contain no detectable amount of polychlorinated biphenyls (PCB's), organic chemicals that can induce dermatitis and liver damage.

Analyses of typical rubber-grade blacks show extremely low amounts of phenols, cyanides, and heavy metals. Selected values for an N-774-type oil furnace black include:

Phenols		0.6 ppm
Lead		2.7 ppm
Antimony	Selenium	less than 0.5 ppm
Arsenic	Thallium	
Barium	Vanadium	
Bismuth	Molybdenum	
Chromium		
Cyanides	Mercury	less than 0.05 ppm
Beryllium	Cobalt	
Cadmium		

Thorough analysis of carbon black is important. The resultant data indicate no health or safety problems and provide assurance that no significant amounts of heavy metals or hazardous substances are being discharged to the atmosphere or into water streams.

This portion of the conference seeks what is known (and what still needs to be known) of the toxicology of significant chemicals, from a biological standpoint, associated with rubber processing operations. Dr. Nau has clinically presented health studies relating to carbon black; we shall also be hearing about carbon black from Dr. Gold and perhaps still more during the academic program. However, interest in carcinogenicity and in inhalation effects justifies further input, even at the risk of some redundancy.

"Petroleum oils and derivative fractions" have been described in the literature as carcinogenic substances. There has been a tendency to include carbon black presumably because it is "derived from" petroleum oils. While petroleum residues are indeed the make fuel for furnace blacks, the carbon black survives flame temperatures in the region of 3000°F (1650°C). Similarly, natural gas is the make fuel for thermal blacks with temperatures about 2400°F (1300°F). The final products are about 99 percent pure carbon. The remainder consists of "ash," "volatile matter," and "extractables." The ash content comes mainly from the inorganic mineral content of the quench water used and has no relationship to carcinogenic materials. "Volatile matter" relates to chemisorbed oxygen present on the carbon surface in the form of carbon-oxygen complexes removable only by heating the black to 1740°F (950°C). These carbon-oxygen complexes are not carcinogens and in any case one can see the inapplicability of the conditions for removal. The "extractables" refer to material removable by long-term continuous reflux extraction by organic solvents such as toluene, benzene, or acetone. Typical extract content of rubber-grade oil furnace blacks is less than 0.1 percent. Medium thermal blacks (N-990 type) have typical extract content of about 0.7 percent and fine thermal blacks (N-880 type) may run about 1.5 percent.

The extractable matter in all furnace blacks and in thermal blacks does contain a number of complex organic compounds including polynuclear aromatics (PNA's), some of which are carcinogenic. This information has been published in various medical journals (cited by Dr. Nau) since 1951. By recent analysis, N-339-type oil furnace black contained 23 ppm 3,4-Benzpyrene and 92 ppm Coronene. N-990-type medium thermal black contained 192 ppm 3,4-Benzpyrene and 472 ppm Coronene. However, and this is the key point, carbon blacks adsorb and bind these PNA's so effectively that they are either not released at all or released so slowly that they are ineffective as carcinogens, based on extensive small animal tests. The carcinogenic compounds themselves, extracted and isolated, produce tumors in small animals. Remember that they are extractable only by severe, long-term chemical treatment. The whole carbon black (which is what is in the worker's environment) causes no tumor or cancer problems when ingested, subcutaneously injected, inhaled, or applied to the skin.

OSHA Standard 1910.93 c-p on "Carcinogens" lists 14 chemicals known to be carcinogens, some of which have been used in the rubber industry. When this standard was devised, mixtures were allowed containing up to 1,000 ppm of 6 of the 14 chemicals and up to 10,000 ppm of the remaining 8. Even if the carcinogenic PNA's on carbon black were desorbed, the amounts would be far below these levels.

Studies of small animal inhalation under extreme conditions led to no abnormality in the lung function. Long-term massive dosage caused some increase in heart-weight and size.

While experimental research has naturally been limited to small animal testing, careful monitoring of the health records of carbon black plant workers has not indicated any out-of-the-ordinary condition. A long-term cancer morbidity and mortality study of carbon black workers led to the conclusion that rates were low relative to other comparable populations. While no evidence of a carbon black health hazard has appeared, we recognize the continuing need for anything that will aid the ecological and environmental containment of the product. The carbon black producers continue to seek improved pelletization to reduce dust, aid in handling, and shorten incorporation times. Packaging and transport vehicles have been upgraded during the past few years. Suppliers encourage and are prepared to advise on adoption of bulk transport, bulk storage, and bulk handling. Totally enclosed systems at consuming plants ease housekeeping tremendously. In plants too small to warrant bulk installation, much can still be done with proper transport, ventilation, lighting systems, and insistence on proper priorities for good housekeeping habits.

Even though we do not visualize carbon black as a causative factor of any illness or injury, preventive medical and occupational safety and health program records from rubber companies should make apparent any associative symptoms.

Just as they have done in the past, the Carbon Black Industry Committee for Environmental Health and the suppliers individually will continue to investigate the safety and health aspects of carbon black and help keep man's house in order.

CARBON BLACK ADSORBATES:
A NEW CARCINOGEN AND OXYGENATED POLYCYCLICS*

Avram Gold, Ph.D.†

Abstract

The polycyclic aromatic and polar fractions of neutral carbon black extract have been analyzed. The structure of a hitherto uncharacterized carcinogen in the polycyclic aromatic hydrocarbon fraction has been elucidated by partial hydrogenation and correlation of the spectroscopic and physical properties of the resulting compound to those of a known compound to establish the structure of the basic carbon skeleton. Analysis of the neutral polar fraction represents the first systematic attempt to determine the constituents of this fraction which, by analogy to the neutral polar fraction of airborne particulates, is expected to have carcinogenic activity. Analysis of the polar fraction was accomplished by preparative high pressure liquid chromatography in conjunction with both high and low resolution mass spectrometry. A number of polycyclic ketones and an anhydride have been identified.

The industrial importance of carbon black and consequent occupational exposure have sparked interest in characterizing its extractable organic components (refs. 1-6). Rubber tire dust, composed largely of carbon black, has also been identified as a component of airborne particulates (ref. 7) in urban locations, especially abutting heavily traveled routes. Because of the widespread exposure to carbon black, the discovery by Monson and Nakano (ref. 8) of the Harvard School of Public Health that rubber workers in jobs with heavy exposure to carbon black experience an increased rate of stomach cancer serves to heighten the importance of studies on carbon black adsorbates.

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*This work was funded by the B. F. Goodrich Company--United Rubber, Cork, Linoleum and Plastic Workers Joint Occupational Health Program.

†Harvard School of Public Health, 665 Huntington Avenue, Boston, Massachusetts 02115.

The organic adsorbates of oil furnace black, a type of carbon black used in manufacturing tires, were investigated. In addition to examining the polycyclic aromatic hydrocarbon (PAH) content of the carbon black, which has been the orthodox approach in evaluating possible carbon black hazard, a systematic effort was made to identify constituents of the neutral polar fraction of carbon black as well. This fraction of carbon black extract would be expected to contain oxygenated polycyclics and other heterocyclic compounds. The neutral polar fraction merits attention since Heuper (ref. 9) and others (ref. 10) have demonstrated that the corresponding extract of airborne particulate matter possesses considerable carcinogenic potency. The composition of organic extractables in airborne particulate matter and carbon black should be very similar since both are derived from the combustion of hydrocarbons. Because of this relationship in composition and the proven carcinogenicity of the neutral polar fraction of airborne particulate matter, the identification and screening of the compounds in the corresponding fraction of carbon blacks would certainly yield environmental carcinogens.

The experimental procedure in the analytical study of carbon black adsorbates is straightforward. The carbon black was extracted with CH_2Cl_2. The crude extract was taken up in benzene, extracted with NaOH to remove acids and phenols, and extracted again with HCl to remove bases. The material remaining in the benzene, the neutral fraction, was then adsorbed on silica and further fractionated by liquid chromatography into saturated hydrocarbon, polycyclic aromatic hydrocarbon (PAH), and polar fractions.

The PAH fraction was separated by preparative gas chromatography (GC) on a 25 percent SE-52 column, 1/4 in. × 15 ft at 270°C. As figure 1 demonstrates, the chromatogram consisted of seven major peaks. Each of these components was collected and characterized by its UV and mass spectrum. For the first six compounds, these data were sufficient for identification.

Figure 2 shows the UV of the first and rather minor component, naphthalene. The spectrum is contaminated with pyrene (which occurred in such a great quantity that it contaminated the collection manifold of the gas chromatograph) but subtraction of the pyrene contribution leaves the proper absorptions for naphthalene. The UV identification of fraction 1 is confirmed by a comparison of the retention time of peak 1 with naphthalene.

The second component was identified as acenaphthylene by its low resolution mass spectrum ($M^{\ddagger}$ 152), UV spectrum (fig. 3), and melting point (92°C). The third component was identified by its UV spectrum as phenanthrene (fig. 4).

Phenanthrene and anthracene have identical molecular weights and fragmentation patterns in the mass spectrometer and also similar retention times by GC. Although they would not have been resolved on the column used for the preparative GC, the presence of anthracene as a significant impurity in compound 3 is ruled out by the UV (fig. 4).

Compounds 4 and 5 were readily identified by UV spectra and low resolution mass spectrometry as fluoranthene (fig. 5) and pyrene (fig. 6). Compound 6 was identified as benzo [ghi] fluoranthene by mass spectrometry ($M^{\ddagger}$ 226), UV (fig. 7), melting point (145°C), and picrate derivative.

Compound 7 could not be identified from its UV or low resolution mass spectrum (fig. 8). The empirical formula, from high resolution mass spectroscopy was $C_{18}H_{10}$ (mass required, 226.0782; found 226.0783). The formula index of Chemical Abstracts led to a reference under cyclopenta [cd] pyrene (fig. 9a) to work by Neal and Trieff (ref. 2) which described an orange, crystalline carcinogenic compound they isolated from carbon black, having a UV (fig. 10) and melting point (165°C) identical to those of compound 7.

This compound, although uncharacterized structurally, had been reported originally by Falk and Steiner in 1952 (ref. 1). Neal tentatively characterized the compound as 3,4 dihydrocyclopenta [cd] pyrene (fig. 9b) rather than the unsaturated compound, which actually makes the Chemical Abstracts reference incorrect. The structural assignment was based on a molecular weight of 228-230 determined by boiling point elevation and a comparison of the UV to that of a compound identified as dihydrocyclopentapyrene in a paper by Wallcave (ref. 11). A comparison of the two UV spectra (fig. 11) immediately rules out the structural assignment by Neal.

Since there are a relatively limited number of reasonable PAH isomers that can be drawn for $C_{18}H_{10}$ and since these systems all contain portions which should be easily hydrogenated, compound 7 was hydrogenated in ethanol over Pd under the assumption that the UV of the remaining aromatic system and the number of hydrogens taken up would give a clue to the structure of the original carbon skeleton.

The hydrogenation product, compound 8, took up two hydrogens, and had a UV spectrum identical to that of Wallcave's compound (fig. 12), closely resembling the UV of pyrene. A literature search under $C_{18}H_{12}$ turned up a paper (ref. 12) in which an unambiguous synthesis of 3,4 dihydrocyclopenta [cd] pyrene was described.

Both compound 8 and the unambiguously synthesized 3,4 dihydrocyclopenta [cd] pyrene gave pale yellow plates from hexane melting at 131°C, positively identifying 8 as the dihydrocyclopentapyrene (fig. 8), which could only have arisen from hydrogenation of cyclopenta [cd] pyrene, the structure assigned to 7.*

Cyclopenta [cd] pyrene is a hitherto unknown carcinogenic PAH that appears to be a major constituent of carbon black, even though benzo [a] pyrene is often absent or a minor compound.

In analyzing the neutral polar fraction, it was necessary first to develop a method for separating the mixture, and second, to work out a procedure for identifying a group of compounds for which no extensive or conveniently tabulated literature exists as it does for PAH's. Separation was achieved by high pressure liquid chromatography (HPLC) using porous reverse phase packing in order to obtain a high capacity column for preparative work. The fractions collected were characterized by low resolution mass spectrometry, IR, and UV. The empirical formulae of the compounds not readily identifiable by these data were determined by high resolution mass spectrometry and the formula index of Chemical Abstracts utilized in conducting a literature search.

The neutral polar fraction had the chromatogram shown in figure 13.

Compound 9 could not be exactly identified. Its empirical formula was established as $C_{18}H_8O_3$. Its IR, with carbonyl bands at 1775 and 1735 cm^{-1} is typical of a cyclic anhydride containing a 6-membered ring (ref. 14). The fragmentation pattern in the mass spectrometer (fig. 14) is completely consistent with this assignment, major fragments being $M^{\dot{+}}$ - 44 for loss of CO_2 and $M^{\dot{+}}$ - 72 for loss of C_2O_3. The fragment at m/e 200 is presumably $C_{16}H_8$, which suggests that 9 is a derivative of fluoranthene or pyrene. The pyrene assignment seems particularly likely since the 6-membered anhydride (fig. 15) could be derived from the oxidation of compound 7.

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*While this work was being reviewed for publication, a paper appeared by Wallcave describing the structural determination of cyclopenta [cd] pyrene in an identical manner (ref. 13). Both papers concur precisely.

Support for this hypothesis can be derived from the identification of naphthalic anhydride (fig. 16) in a preliminary workup of the bicarbonate-soluble acid fraction of the carbon black extract by HPLC. The appearance of the anhydride in the acid fraction presumably resulted from hydrolysis to the di-acid and extraction by base, then dehydration during acidification of the basic extract prior to reextraction into organic solvent during the workup procedure. The identity of naphthalic anhydride was established by determining its empirical formula ($C_{12}H_6O_3$ by high resolution mass spectrometry), and by its mass spectral fragmentation pattern (fig. 16) and its IR spectrum (ν_{co} 1775, 1741 (ref. 15)). The naphthalic anhydride might be an oxidation product of acenaphthylene, one of the PAH constituents of the carbon black extract.

Compound 10 was identified as phenalenone by its UV (fig. 17) (ref. 16) and IR (ν_{co} 1650 cm^{-1}) spectra (ref. 17).

The empirical formula of compound 11 was established as $C_{15}H_8O$, and through the literature (ref. 18) its identity was established as 4 H-cyclopenta [def] phenanthren-4-one (fig. 18). The carbonyl frequency in the IR (1725 cm^{-1}) is consistent with the 5-membered cyclic conjugated ketone.

Similarly compound 12 was shown to have the formula $C_{19}H_{10}O$ and its identity was established through its UV and mass spectra (fig. 19) as 6H-benzo [cd] pyren-6-one (ref. 16). A sufficient amount of 12 was obtained to purify for a melting point which at 252°C is in accord with published data as well as the carbonyl band in the IR at 1656 cm^{-1} (ref. 19).

Of the compounds identified in the neutral polar fraction, only phenalenone appears to be well known, and the carcinogenic properties of these compounds do not appear to have been examined.

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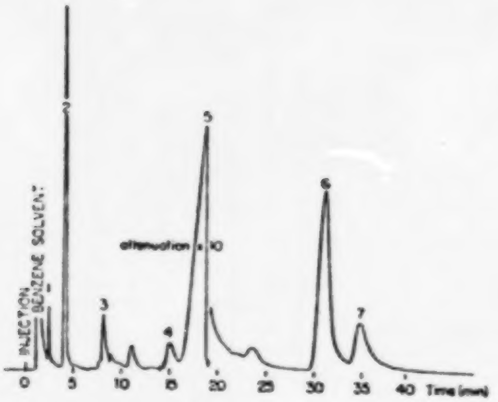


GC trace of PAH fraction
column: 15' x 1/4" 25%SE-52 on ChromosorbW
temp= 225°

Figure 1.

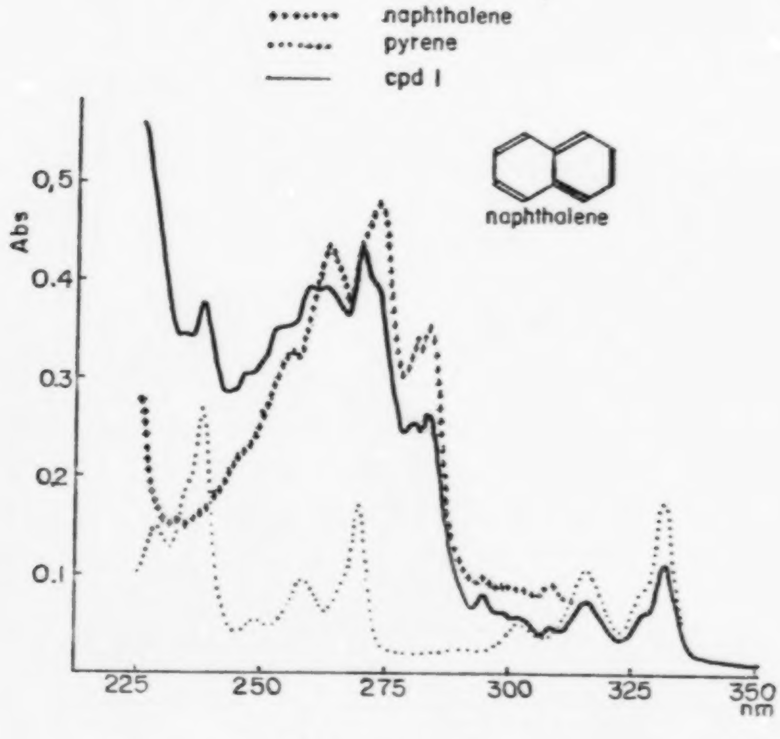


Figure 2.

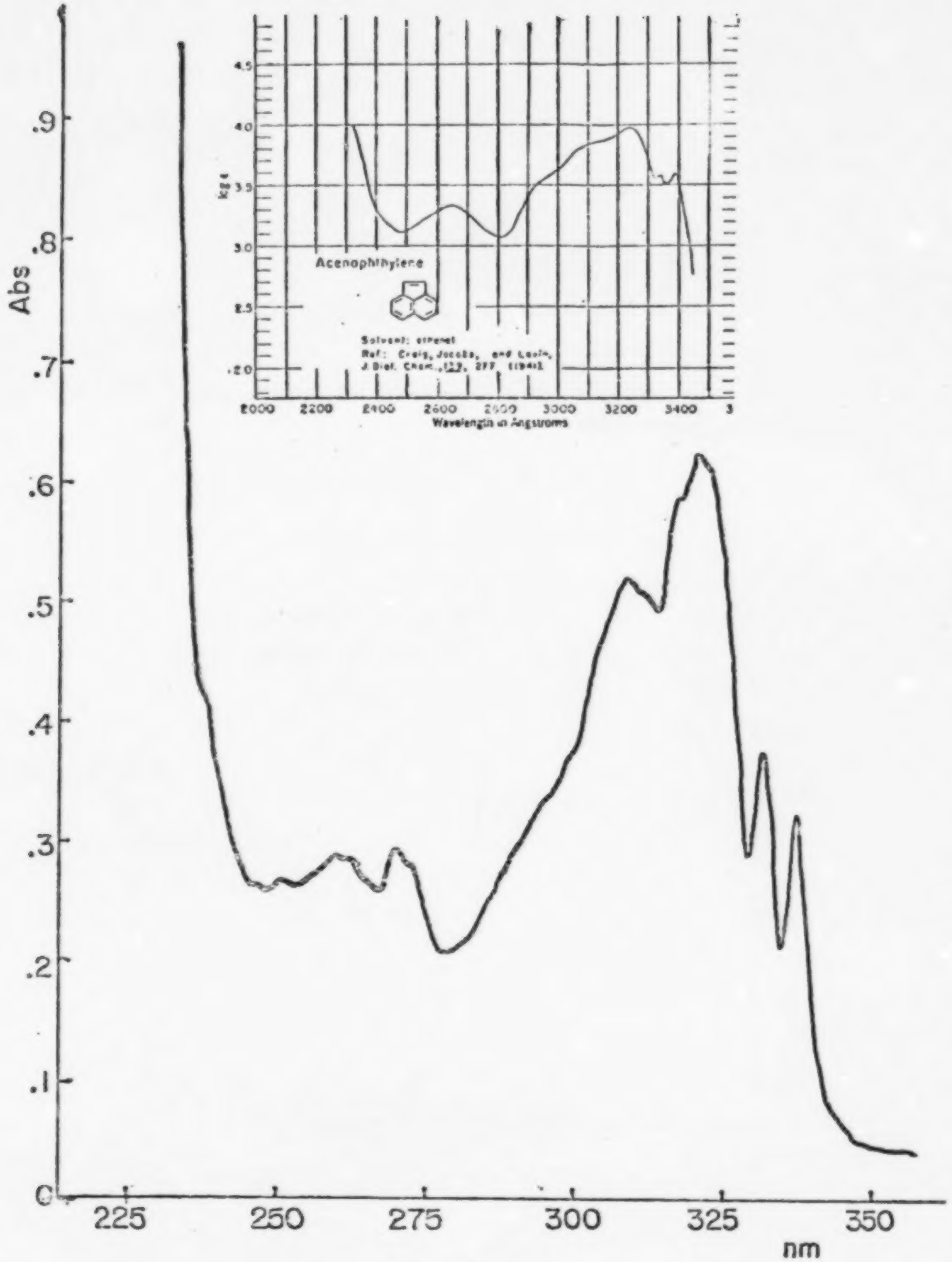
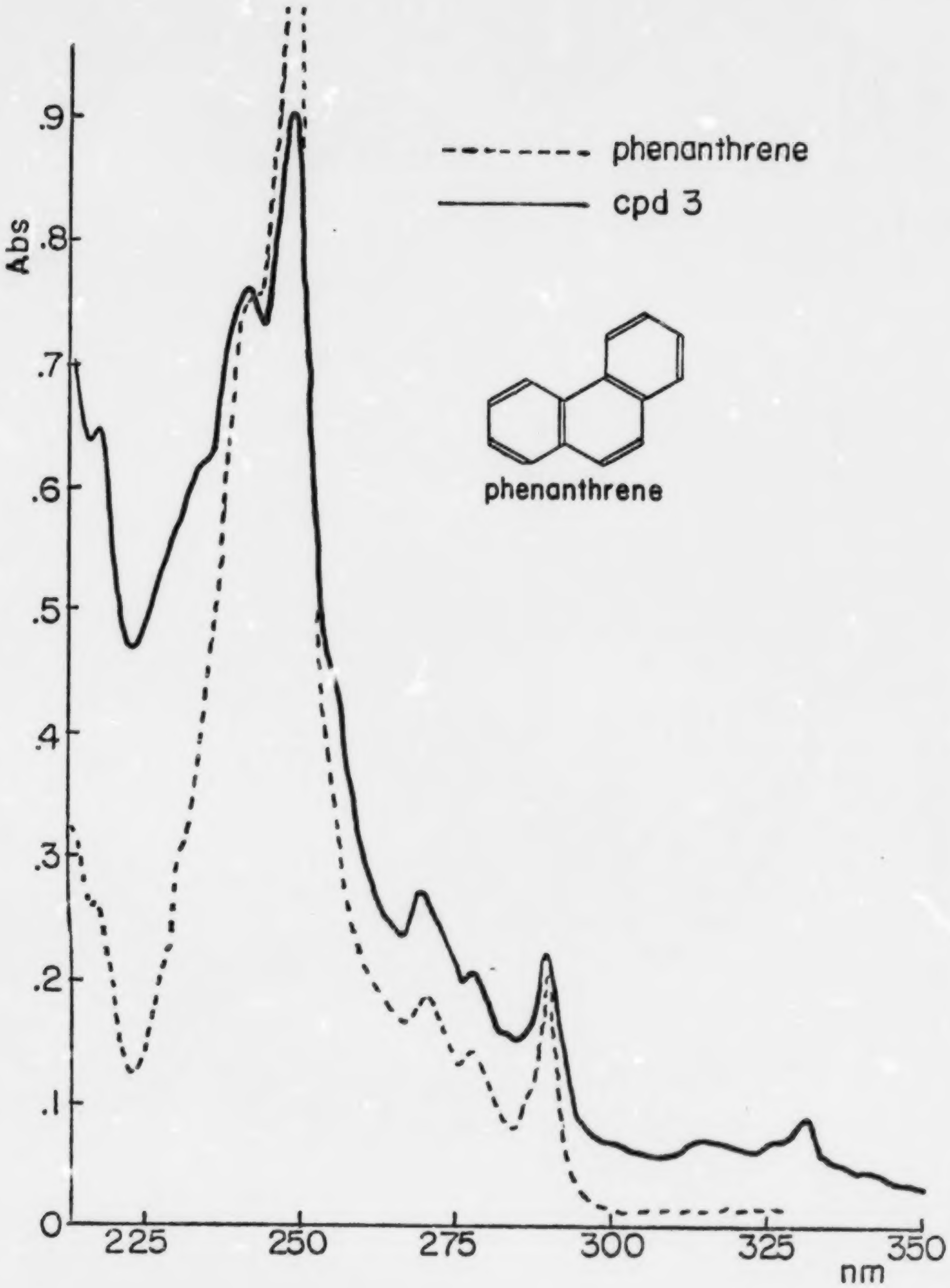

Abs
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
225
250
275
300
325
350
nm
log ε
4.5
4.0
3.5
3.0
2.5
2.0
2000
2200
2400
2600
2800
3000
3200
3400
3
Wavelength in Angstroms
Acenaphthylene
Solvent: ethanol
Ref: Craig, Jacobs, and Lavin,
J. Biol. Chem., 139, 277 (1941)

Figure 3.



Abs
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275
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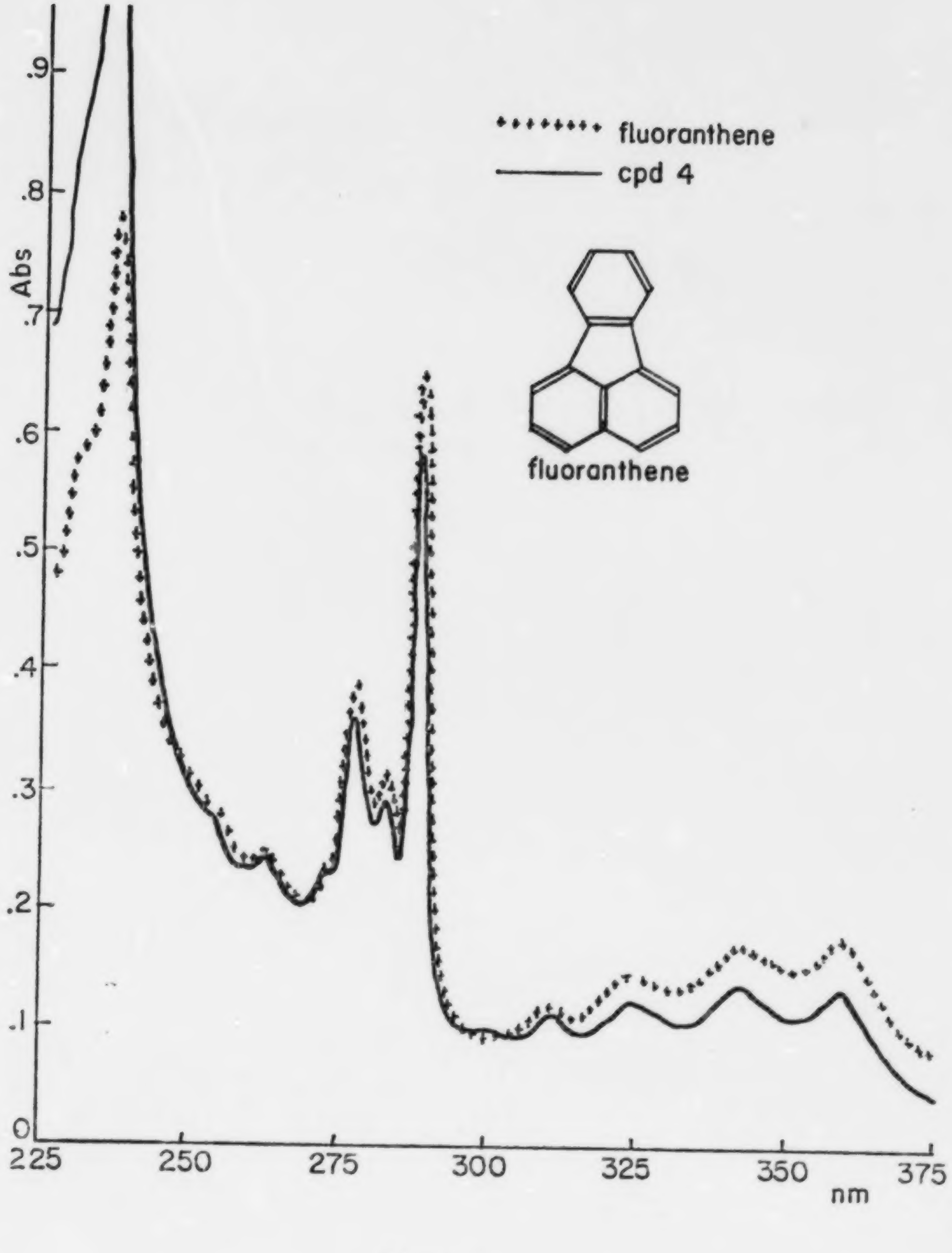
350
nm
phenanthrene
cpd 3
phenanthrene

Figure 4.



Abs
.9
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0
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275
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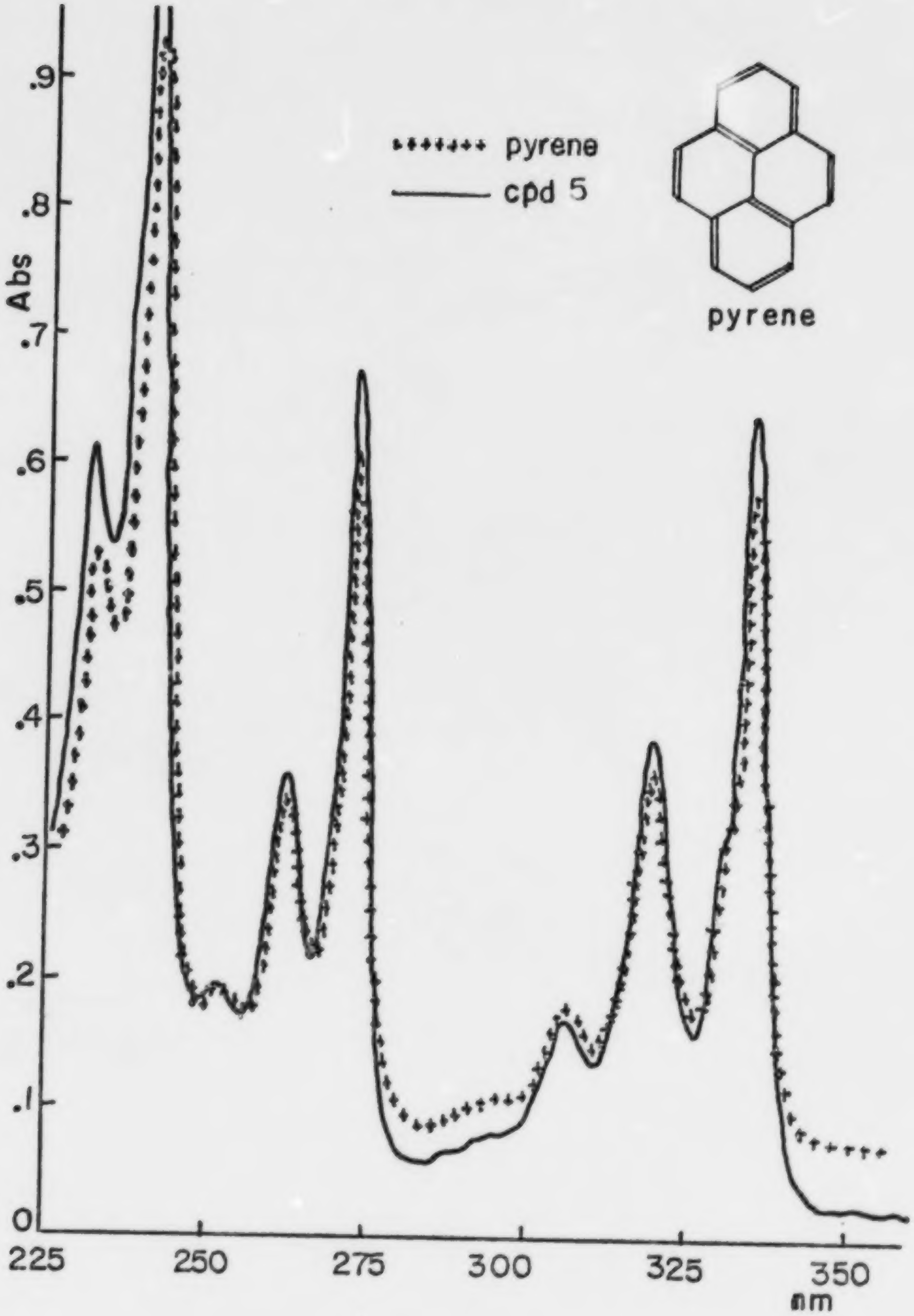
375
nm
++++++++ fluoranthene
cpd 4
fluoranthene

Figure 5.



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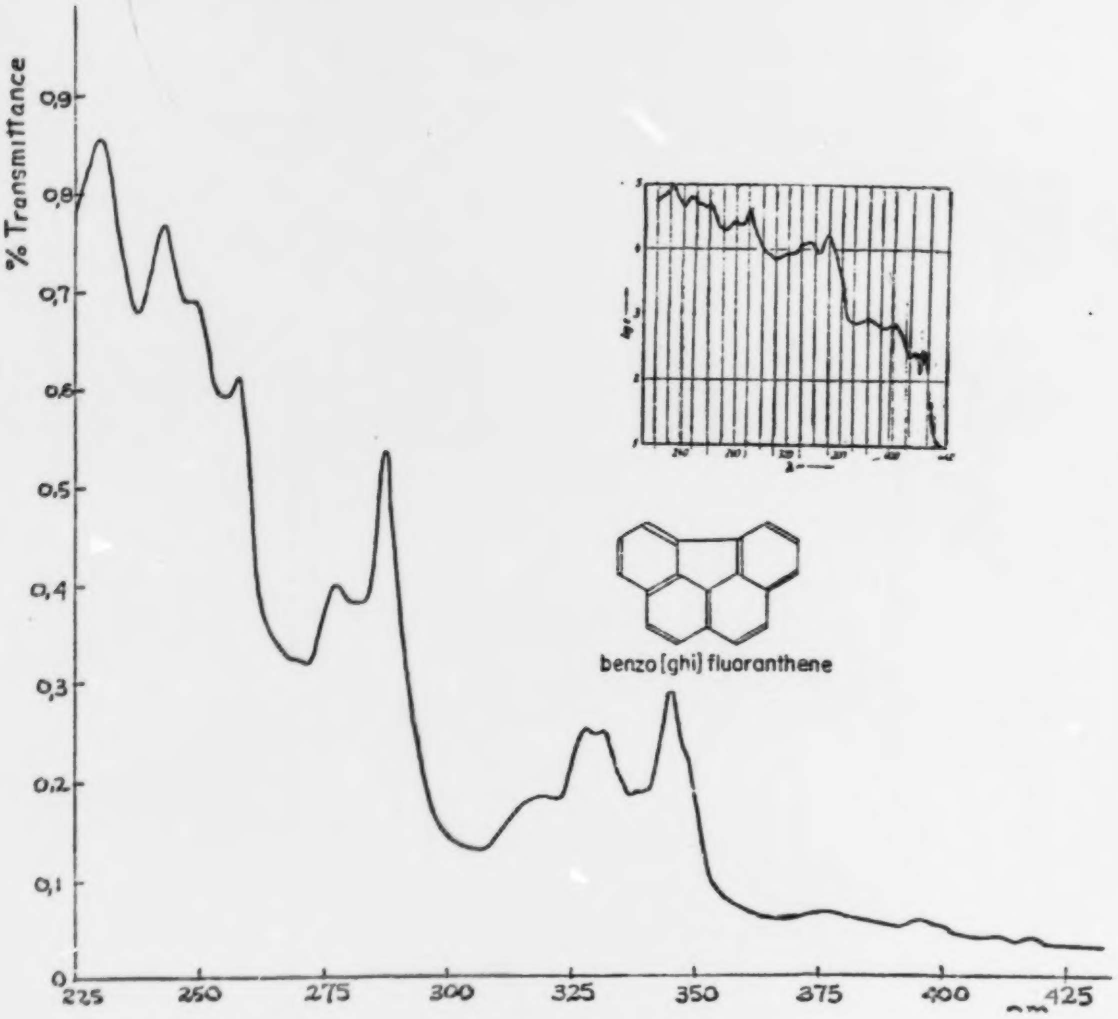
% Transmittance
0,9
0,8
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0,6
0,5
0,4
0,3
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0,1
0
225
250
275
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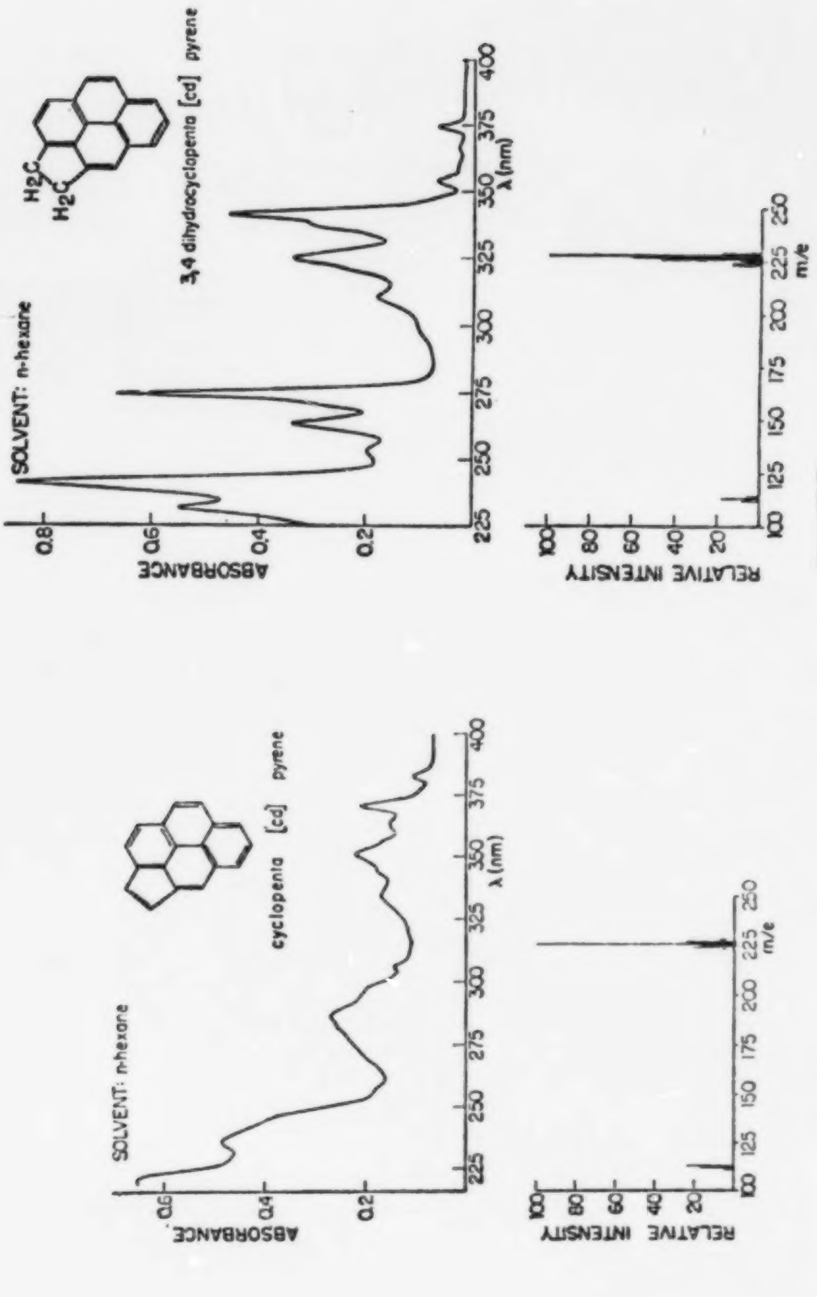
325
350
375
400
425
nm
benzo [ghi] fluoranthene

Figure 7.

SOLVENT: n-hexane
ABSORBANCE
0.8
0.6
0.4
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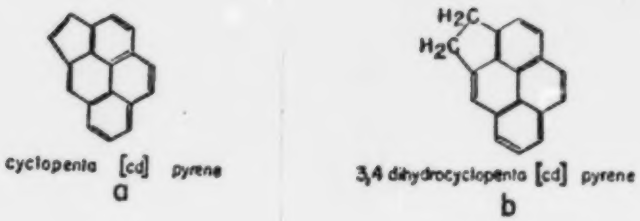
225
250
275
300
325
350
375
400
λ (nm)
H_2C
H_2C
3,4 dihydrocyclopenta [cd] pyrene
RELATIVE INTENSITY
100
80
60
40
20
100
125
150
175
200
225
250
m/e
SOLVENT: n-hexane
ABSORBANCE
0.6
0.4
0.2
225
250
275
300
325
350
375
400
λ (nm)
cyclopenta [cd] pyrene
RELATIVE INTENSITY
100
80
60
40
20
100
125
150
175
200
225
250
m/e

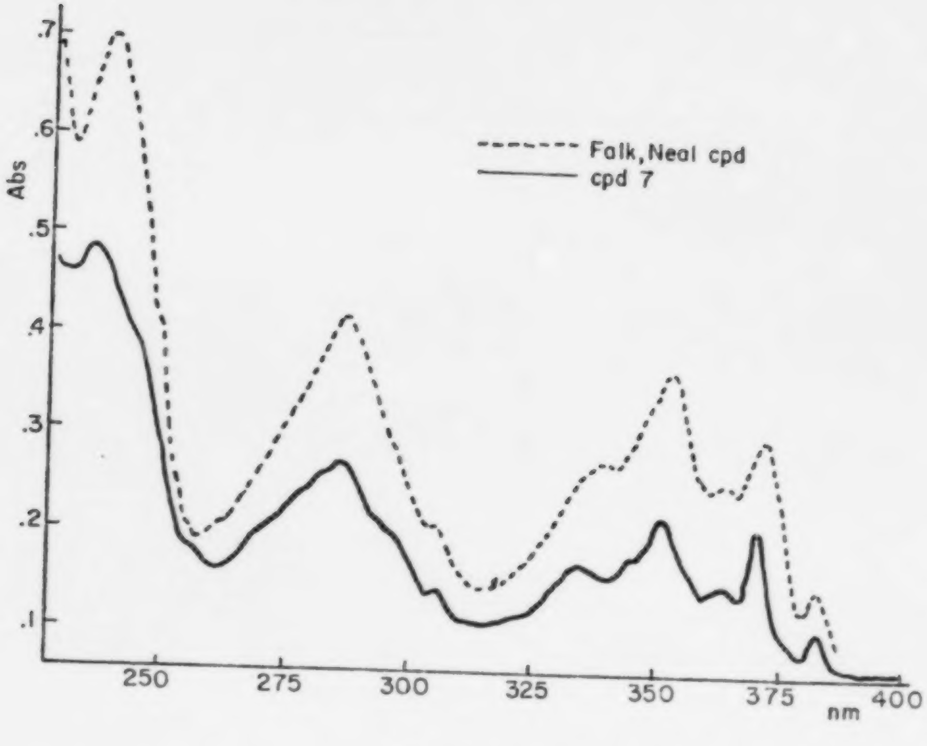
Figure 8.



cyclopenta [cd] pyrene
a

3,4 dihydrocyclopenta [cd] pyrene
b

Figure 9.



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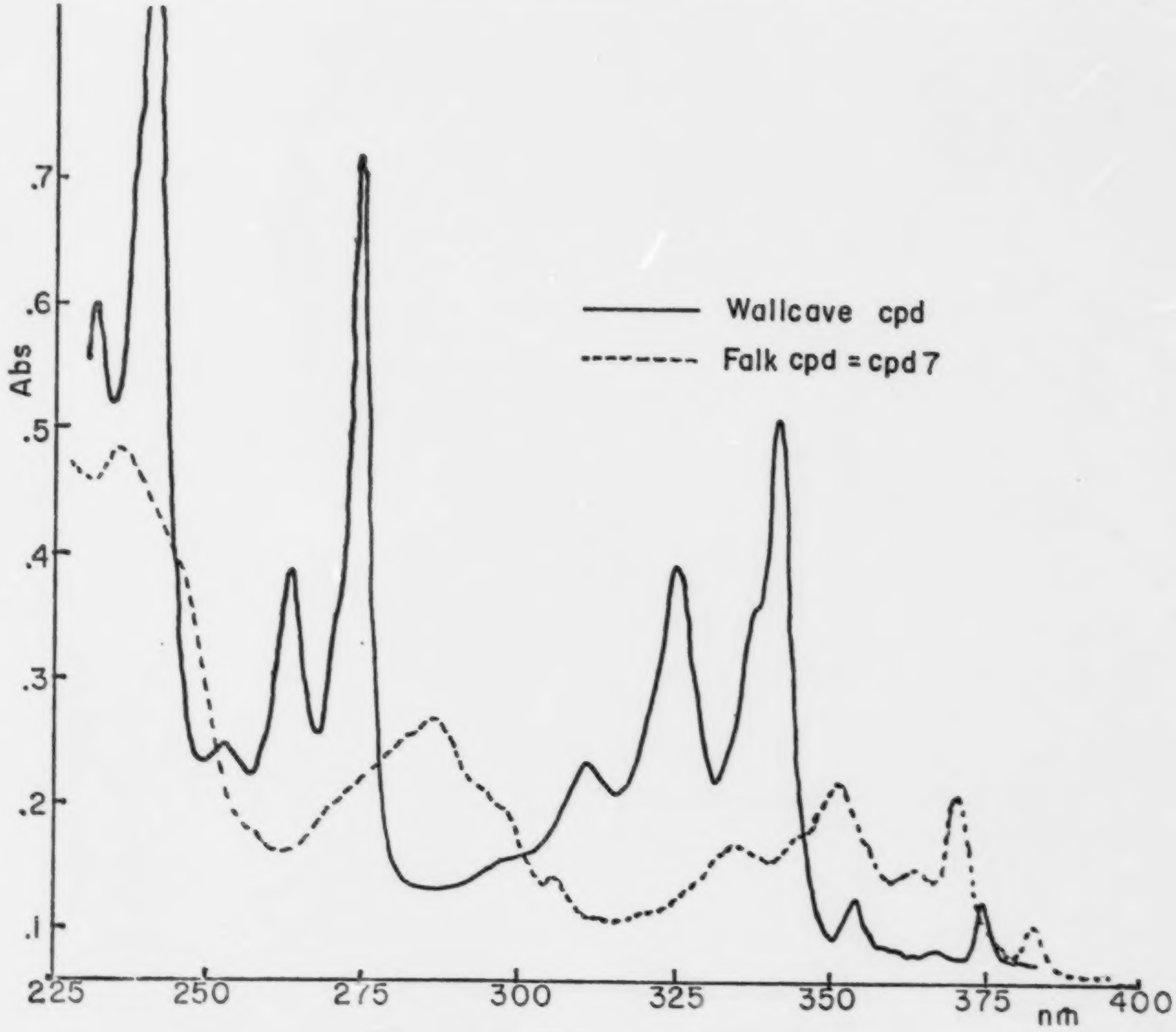
Abs
.1
.2
.3
.4
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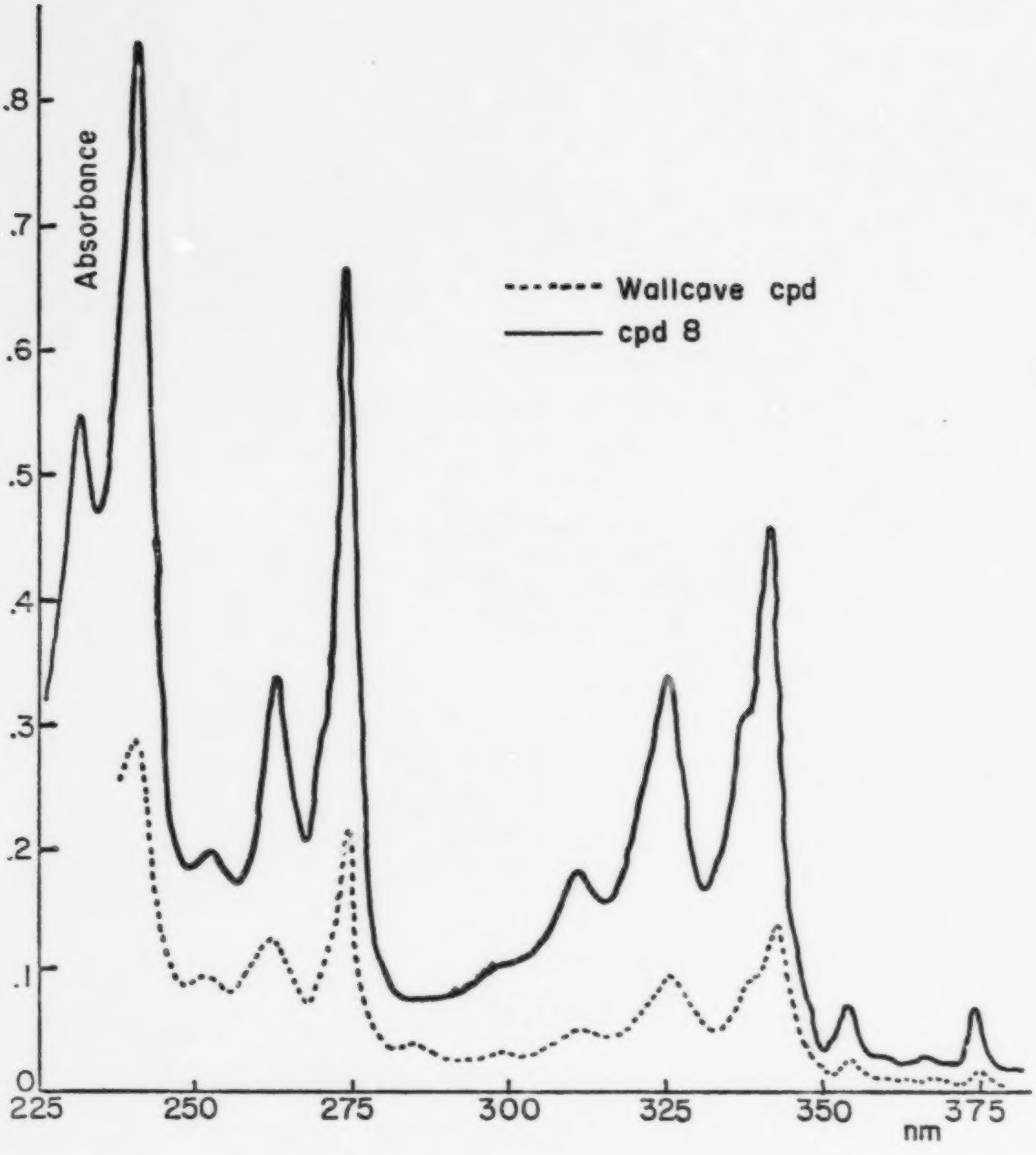
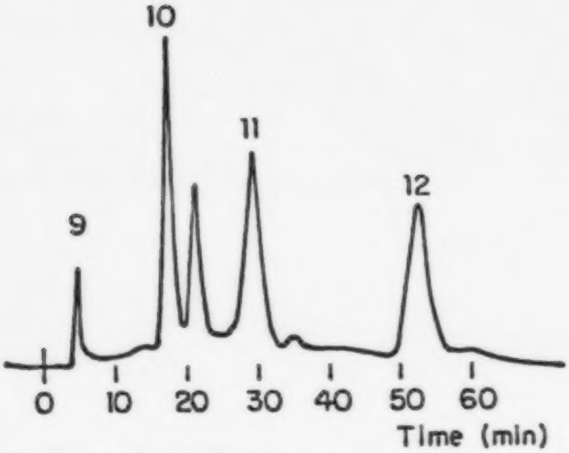
225
250
275
300
325
350
375
400
nm
Wallcave cpd
Falk cpd = cpd 7

Figure 11.



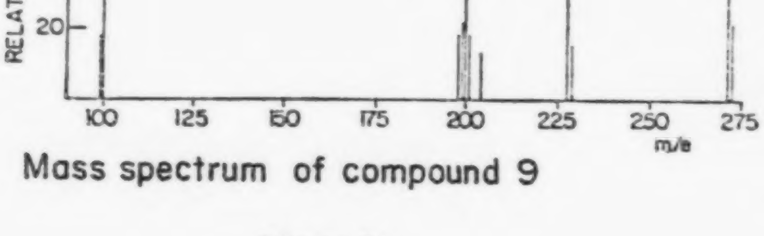
Absorbance
.8
.7
.6
.5
.4
.3
.2
.1
0
225
250
275
300
325
350
375
nm
Wallcave cpd
cpd 8

Figure 12.



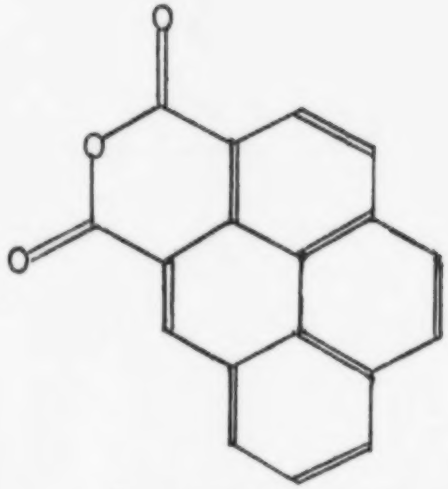
Liquid chromatogram of neutral polar fraction
column Octadecyl Sil X I 4.6mm x Im
eluant 30% water - 70% methanol

Figure 13.



Mass spectrum of compound 9

Figure 14.



Compound 9

Figure 15.

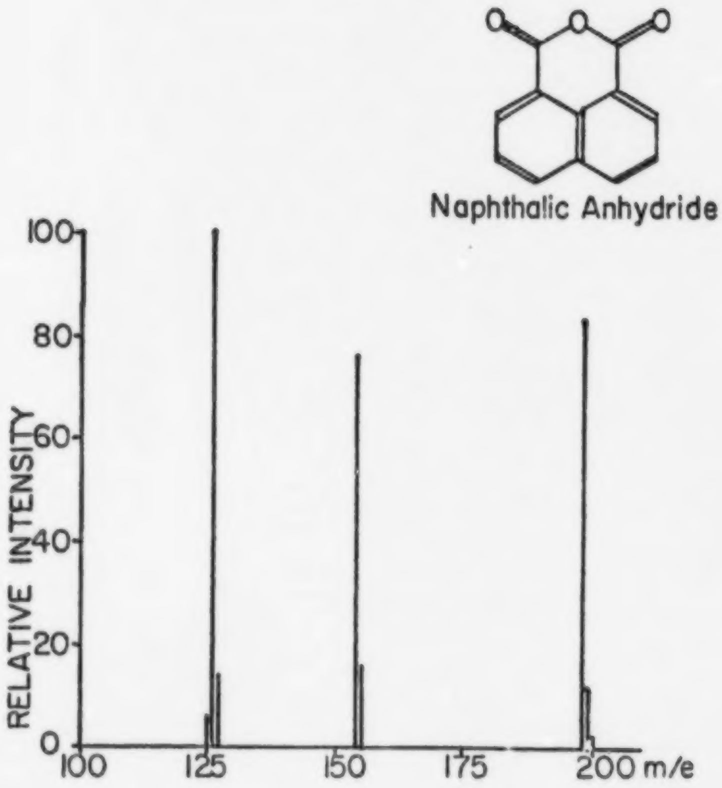
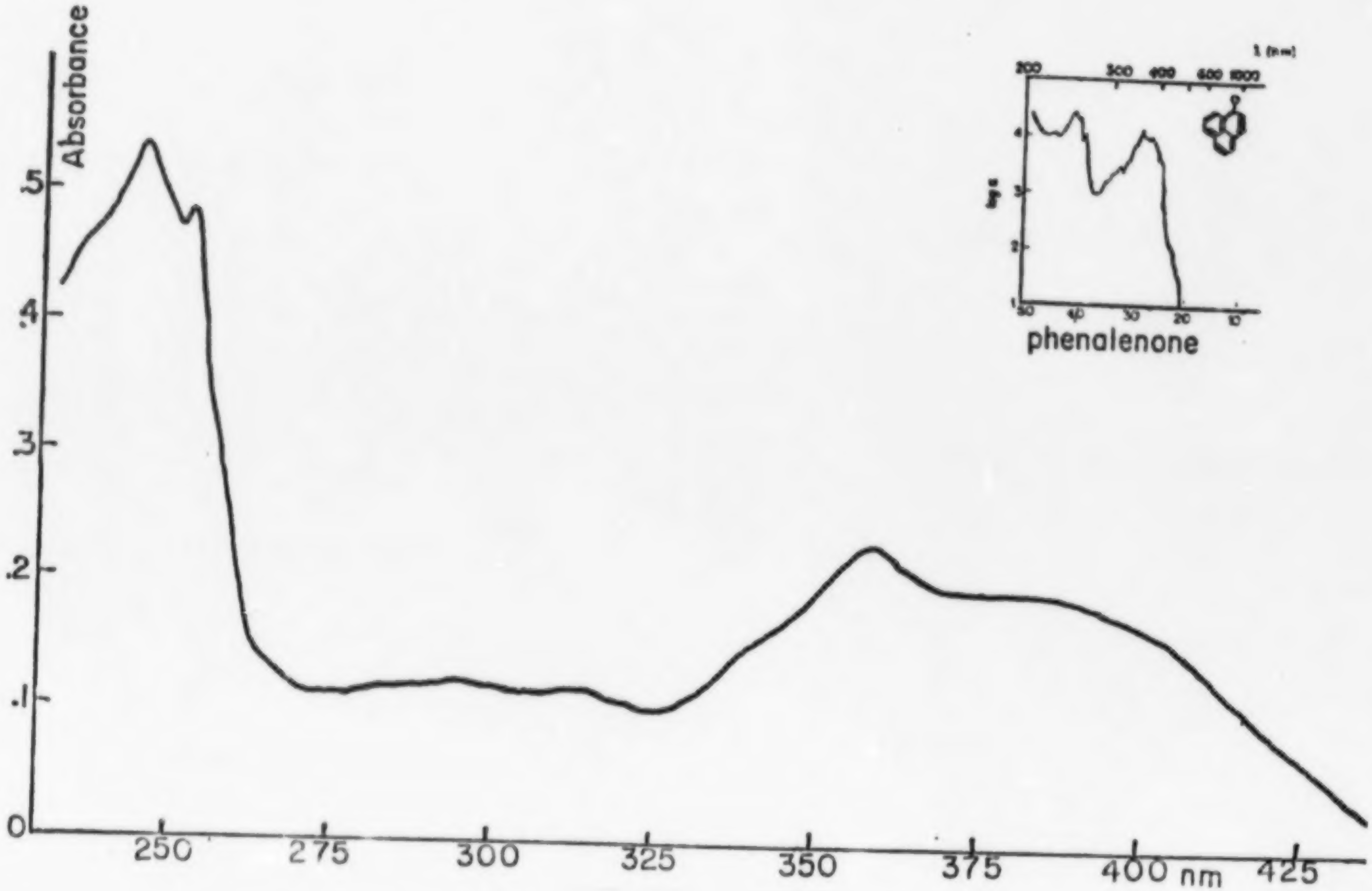


Figure 16.


Absorbance
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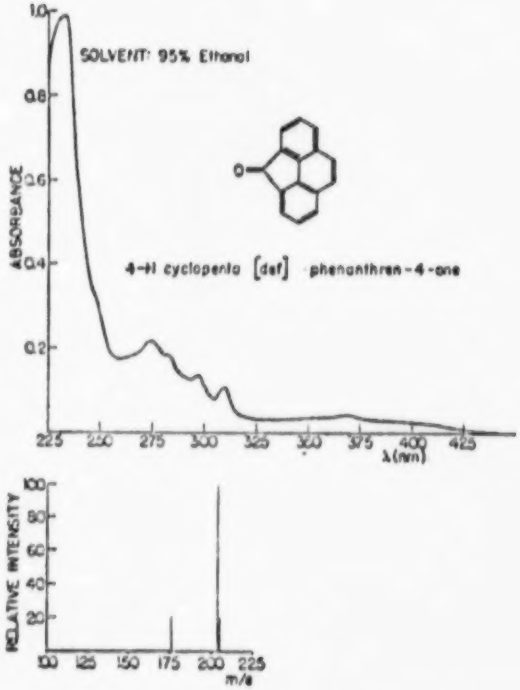
.4
.3
.2
.1
0
250
275
300
325
350
375
400 nm
425
λ (nm)
200
300
400
600
1000
log ε
4
3
2
1
50
40
30
20
10
phenalenone

Figure 17.



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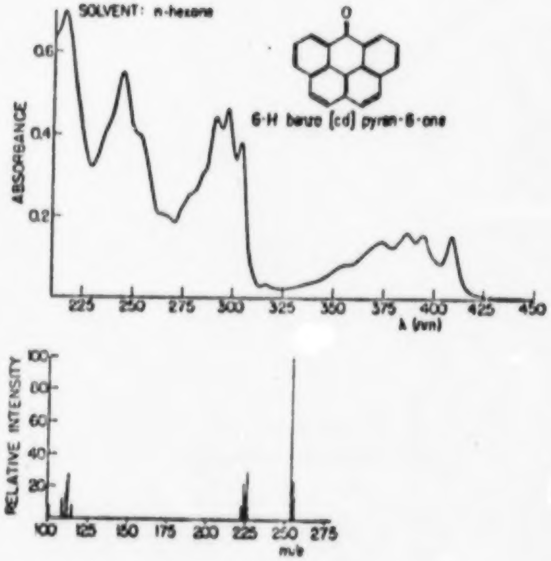

Figure 19.

DISCUSSION

Following papers presented by Dr. Nau, Mr. Collyer, and Dr. Gold

MR. RICHARD HUNTINGTON (Cooper Tire and Rubber, Findlay, Ohio): The question that really comes to my mind is, are these cancers, these carcinogens that are produced, benign or malignant? Were they active or passive?

DR. GOLD: I am not an epidemiologist, but the researchers have this to say in epidemiological studies with work in the rubber tire industry; this is a lung cancer and stomach cancer. At least people die from it.

MR. HUNTINGTON: Is carbon black an antidote for these carcinogens? Can you take active carbon and counteract the action of these nuclear hydrocarbons so that it does not affect anybody?

DR. GOLD: I did not state that carbon black caused cancer. However, among rubber tire workers with heavy exposure to carbon black--they are exposed to other things too--and also among the curing room workers in the rubber tire plant who may be exposed to compounds which are desorbed by steam distillation from rubber blacks, an increased rate of stomach cancer was exhibited in the processing areas exposures, and lung cancer in the curing room exposures.

Now the carbon black and the compounds absorbed thereon are among the exposures that these people are undergoing. Under the circumstances it tends to make the carbon black somewhat suspect, although it is not proof that carbon black or compounds thereon are causative.

I am not the author of the epidemiological paper, and I am not a medical doctor. I am not an epidemiologist, so I can't really defend the work, except to say that, as far as I know, their results are significant. There was a significant increase in the cancer rate among these workers, and the workers did have an exposure to carbon black or to the compounds on the carbon black. Under those circumstances, it would seem to be worth studying what is there. I do not know anything about any other curative properties of carbon black.

DR. CARL A. NAU (Texas Tech University, Lubbock, Texas): I would like very much to comment on that. My experience deals with a lot of the blacks. I have not seen tumors in people who have been exposed to carbon black. I have taken extract off of carbon black. You ask if these are malignant tumors. That is hard to define. I can just tell you that if I take the benzene-extracted material, and paint it on the skin of mice, I can get a tumor, but it does not metastasize. This is generally thought to be a requirement of a malignant tumor. The tumor stays right at that spot and grows at that spot. But it does not show up elsewhere in the body.

MR. HUNTINGTON: In other words, it is benign?

DR. NAU: In that sense, if it does not metastasize, it is benign, yes, but it grows bigger and bigger.

CHAIRMAN MCCORMICK: I am not a physician but the word "cancer"--per se--means "malignant." Now if you want to say tumor, then I think there are questions as to whether or not it is benign or malignant. I think it is generally recognized that it is a malignant tumor, yes.

DR. NAU: May I make a definition of malignant versus benign tumor, but I am not sure the language will be understandable. A malignant tumor is a tumor in which the cells have some pleomorphism; they show lack of regularity; they show variations in nuclear size and staining properties. Generally, to be defined as malignant the tumor must be transplantable. I absorbed on carbon black a known carcinogen. The skin application or the injection of the absorbed known carcinogen was ineffective; so it was my conclusion that the carbon black absorbed it so firmly that it was not effective as a carcinogen after it was absorbed.

DR. MARS Y. LONGLEY (SOHIO, Cleveland, Ohio): I have a couple of questions here--one for Dr. Nau. One thing I want to ask is, has anybody tried to extract the hydrocarbon from carbon black, let's say with lung exudate or pulmonary fluid or tissue?

DR. NAU: All we did was use human blood plasma.

DR. LONGLEY: But no pulmonary fluid?

DR. NAU: I do not know how the pulmonary fluid would differ from blood plasma. I really am not qualified to answer that, but I would assume they would be identical.

DR. LONGLEY: And on your work with monkeys, how many animals were you using for exposure?

DR. NAU: Thirty-five.

DR. LONGLEY: That were exposed?

DR. NAU: Yes, 35.

DR. LONGLEY: How much?

DR. NAU: That was 1.6 mg/m^3.

DR. LONGLEY: For 1,500 hours?

DR. NAU: I will have to go to the paper. The number of hours was quite a few thousand.

MR. MCCORMICK: I think it said 13,000.

DR. LONGLEY: I do have some question about the extractions of some of these compounds-in the body tissue fluid. I am not quite in agreement with Mr. Collyer when he says that further experimentation would be redundant.

MR. HARRY J. COLLYER (Cabot Corporation, Billerica, Massachusetts); I would like to make one more comment about the subject of polynuclear aromatics which are presumably dangerous. This is on the question of malignancy or benignancy. I am not a medical doctor, but have taken a 4-month course on my own. There is a term that is used in the medical literature--neoplastic. A polynuclear aromatic can be neoplastic, which I believe means that it has the ability to form a benign tumor. In other words, it is tumorogenic but not carcinogenic. Some of these PNA's that Dr. Gold referred to and that other people have referred to are neoplastic but not carcinogenic.

MR. MCCORMICK: The term neoplastic refers to both. It includes both, either malignant or benign. It is a general term meaning "new growth" and is undefined as respect to malignancy.

DR. GOLD: I have one question I would like to address to Dr. Nau about the epidemiology on carbon black workers, and that was whether or not he has listed cancer by categories or by types of cancer. I think it has been the experience of Monson that certain types of cancer, such as stomach cancer or lung cancer, can be in excess of what is normally expected, and that fact may be hidden in a low overall cancer rate. So I wonder if his cancer rate is broken down by types of cancer?

DR. NAU: I will have to refer to the publications which were submitted by the epidemiologists who made these studies.

OBSERVER: I had a question of Mr. Collyer. Why did you feel that any work would be redundant as mentioned in the discussion? I think we encourage further work, and if I interpret the gentleman's question, I don't think that Mr. Collyer said that further work was redundant.

MR. COLLYER: I did not state that further work was redundant. My remark about possible redundancy meant that I was repeating in my paper what Dr. Nau had just so ably reported.

MR. LUCIAN E. RENES (Phillips Petroleum Company, Bartlesville, Oklahoma): At the risk of getting highly involved in a subject on which I am not qualified to speak, I would like to make a few comments.

First of all, we have analyses made on 10 commercial blacks that we manufacture. They were made for us by the Eppley Institute for Research in Cancer. It is true what Dr. Gold has said. Cyclopenta (cd) pyrene is present, at least in the carbon black samples examined for us. At the present time cyclopenta (cd) pyrene is not a proven carcinogen. If Dr. Phillipe Shubik, Director of the Eppley Institute, said it was a proven carcinogen, I would believe him, but it is not a proven carcinogen.

Second, I think the studies made by Dr. Gold and the identification of many of the oxygenated compounds, are a very highly thought-out scheme of events. We ourselves have also tried to do that, and unquestionably we have not carried out and identified all the various materials that are present on carbon blacks. I think this would be just an endless job. We have identified the major polycyclic aromatic compounds by class, and by class I mean three-ring, four-ring, five-ring, and six-ring compounds.

Dr. Wallcave of Eppley Institute has shown in the case of our furnace blacks that the only carcinogen, the only proven carcinogen, present, on these blacks is 3,4 benzpyrene.

MR. MCCORMICK: And this is proven--human, you mean?

MR. RENES: This compound and several other polycyclic hydrocarbons have been tested by a variety of experimental procedures and are considered to be carcinogens by authorities in this field such as Dr. Phillipe Shubik. There is one other thing that I want to mention. In connection with these analytical findings, I think it is important not to lose sight of the results of Dr. Nau's studies on animals that were exposed to carbon blacks for periods from one-half of their lives to a lifetime; they developed no adverse effects. Furthermore, the individuals working in the carbon black industry are exposed only to carbon black. The medical examination of those peoples has, as of this time, not revealed any excessive numbers of any kind of cancers, not only gastric cancers, but also pulmonary cancers. This is a very important finding. Perhaps, it points out the difficulties of working with a population such as that in the rubber industry, where there are mixed exposures to a variety of agents in addition to carbon blacks.

I agree with some of the comments that were made by other people that further work needs to be carried out on carbon blacks. One important finding that Dr. Nau has made, on which he did not elaborate in the slides, is the elution studies in the carbon blacks made a number of years ago. He had placed carbon black as well as some materials containing carbon black into a variety of different physiological fluids and kept them in those particular fluids for several days at elevated temperatures, and was not able to elute any 3,4 benzpyrene from the whole carbon black by means of these physiological fluids. There is another thing that I would like to refer to, but this becomes highly complicated; that is, work that was done by Dr. Phillipe Shubik of Eppley Institute for an entirely different purpose and which was not related to carbon blacks. A number of years ago, Dr. Shubik undertook a project to investigate the carcinogenicity of aromatic hydrocarbons for the American Petroleum Institute, Division of Medicine and Health.

This was a study that he carried out very carefully. He was trying to show the means by which it is possible to induce pulmonary cancer in animals without first introducing trauma into the lung.

In doing this particular work, one of the things he did do was to obtain some carbon black (a channel black) that was presumably free of carcinogens. He deposited and adsorbed on the carbon black some methyl cholanthrene. Incidentally, the compound does not occur freely in nature. It is a synthetic polycyclic aromatic hydrocarbon, which is also a very powerful carcinogen. He found that on intubating the carbon black on which he had adsorbed 50 percent by weight of the carcinogen, he was able to induce cancer in the lungs of these particular animals that had all the characteristics of human cancer.

He was able to show that as the total amount of carcinogen that was deposited on the carbon black is intubated into a succeeding series of animals, in gradually reduced amounts, the point is reached at which no lung cancer was formed from the contact with the material. The amount of carcinogen that Dr. Shubik found to produce animal effects in the lung structure was far greater than that is present in the carbon blacks that you have been hearing about over here.

Dr. Wallcave, who examined our carbon blacks found that the only proven carcinogen that was present on the blacks was 3,4-benzpyrene. It varied from 0.8 ppm to a level slightly under 7.0 ppm. One of the commercial blacks contained zero amount of 3,4-benzpyrene. Dr. Wallcave tells me that the sensitivity of the analytical procedures that he used were capable of detecting down to the level of 10 ppb; philosphically, that is zero.

(For further information on the effects of carbon black, see the paper by Mr. Lucian Renes in the section of these proceedings entitled Submitted Papers Not Presented at the Conference.)

MR. MCCORMICK: Regarding the occupational discussion of cancer, there are two basic philosophies among the experts. One philosophy goes somewhat like this. If one is able to produce a cancer, a malignant tumor, in any animal of any species, no matter what it is, this is a potential human carcinogen and you should not further insult humanity with that particular compound. There are literally thousands of compounds, many compounds, which may have been investigated over many years and which do produce cancers in animals. This is the so-called "no-threshold" level for carcinogens.

The other philosophy is somewhat in opposition to this. We say that there is a threshold for all carcinogens and it becomes a matter of defining what it is, and of defining the conditions under which the insult to the human species may occur and carcinogens furnish physiological responses. Therefore, the no-threshold philosophy should not be accepted.

ELASTOMERS IN THE HEALTH INDUSTRIES

Samuel Koorajian, Ph.D.*

Abstract

Elastomeric materials have been used extensively in the health industries not only in the drug field but also in medical devices. The types of elastomers most commonly used, natural rubber, latex rubber, and silicone rubber, along with typical formulations of these rubbers will be reviewed and discussed. Silicone rubber has wider application in medical devices than natural rubber, which is used extensively in the drug field. The application of elastomers in medical devices is critical as many of them are used in lifesaving devices and in devices used to treat life-threatening conditions. The toxicological testing of these rubbers, their components, and the relevance of the testing procedure to the end use of these materials will be discussed. The toxicity of elastomers in the health industries is more critical and refined than that in the rubber industry in general.

Some potential and real problems encountered with elastomers used in the health field will be briefly reviewed, specifically the failure of silicone rubber in heart valve prostheses. The conditions leading to this failure, the cause of this failure, and the resolution to this problem will be presented.

INTRODUCTION

Rubber or elastomers have played and will continue to play a vital role in the health-related industries. The requirement for flexible materials with the unique properties of elastomers has grown rapidly in this field over the past 15 to 20 years. The types of elastomers used are diverse and include natural, synthetic, latex, and silicone rubbers, polyurethanes, etc. The use of elastomers and natural rubber in the health field is small in comparison to use in the consumer field in general. It could best be measured in the thousands of pounds as opposed

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*Edwards Laboratories, Division of American Hospital Supply Company, Santa Ana, California 92702.

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to tons and would not be considered a major consumer material by standards set by the large rubber companies.

The medical uses of silicone elastomers find their greatest application as blood tubing, catheters, heart valve occluders, oxygenator membrane, soft tissue augmentation and repair, coating for pacemaker electrodes, and adhesives. Natural and latex rubbers are most commonly used in the health field as tubing, catheters, tips for syringe plungers, bottle stoppers, baby bottle nipples, surgeons gloves, and prophylactics. A few of the applications of these materials are shown in figures 1 and 2.

The type of toxicological testing required prior to the use of some materials in the health field is controlled by government recognized organizations. These tests are somewhat different than those used to determine the safety of a material in an industrial application and are a more sensitive measure of the potential hazard of a material. Some of these test methods will be discussed along with the results observed when elastomers are subjected to these tests.

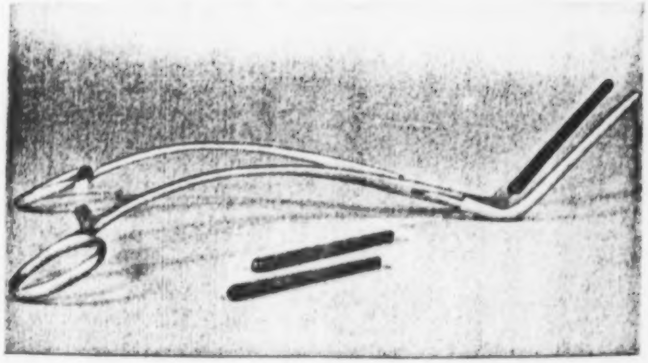
Silicone rubber has been used extensively in the medical field, particularly in devices, as it has demonstrated excellent biocompatibility (ref. 1). A notable failure of this material when used in a medical device will be discussed in detail. This failure was unpredictable as it only became apparent after clinical usage.

FORMULATIONS

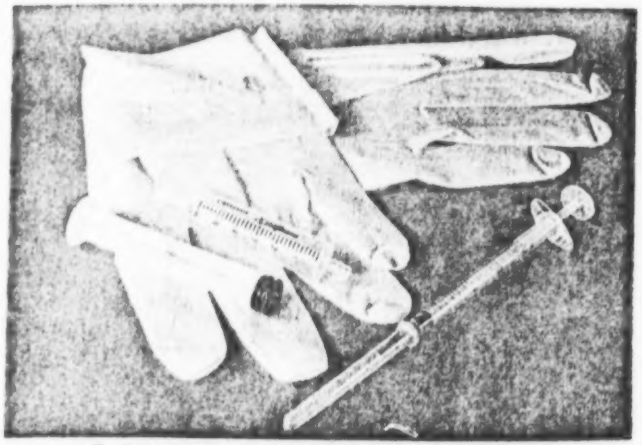
Natural and Latex Rubber

The basic components of natural and latex rubber are the crepe or latex, the vulcanizing agent, sulfur, and heat. This will yield an elastomeric material that will have limited value and application. In order to obtain a useful material other ingredients must be added to the formulation. The selection and addition of these other ingredients will be dictated by the desired properties along with the end use of the elastomer. The additives fall into several categories and include antioxidants, accelerators, fillers, ultra-accelerators, antiozanants, activators, blowing agents, stabilizers, plasticizers, and mold release agents and pigments.

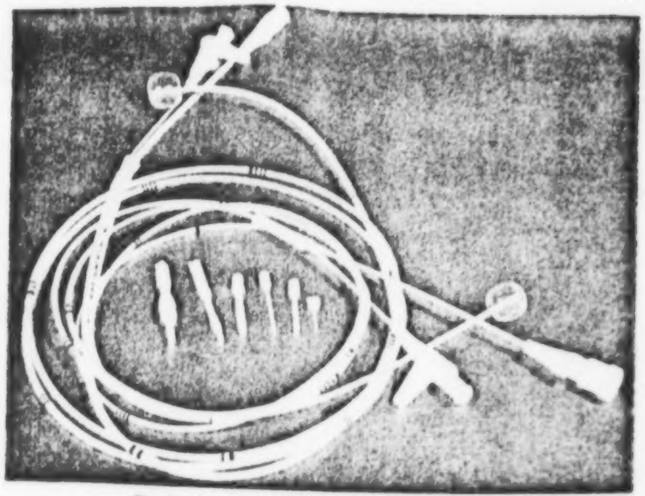
A. Natural rubber bottle stoppers



B. Natural rubber sponge and fluid filled inserts for surgical clamp

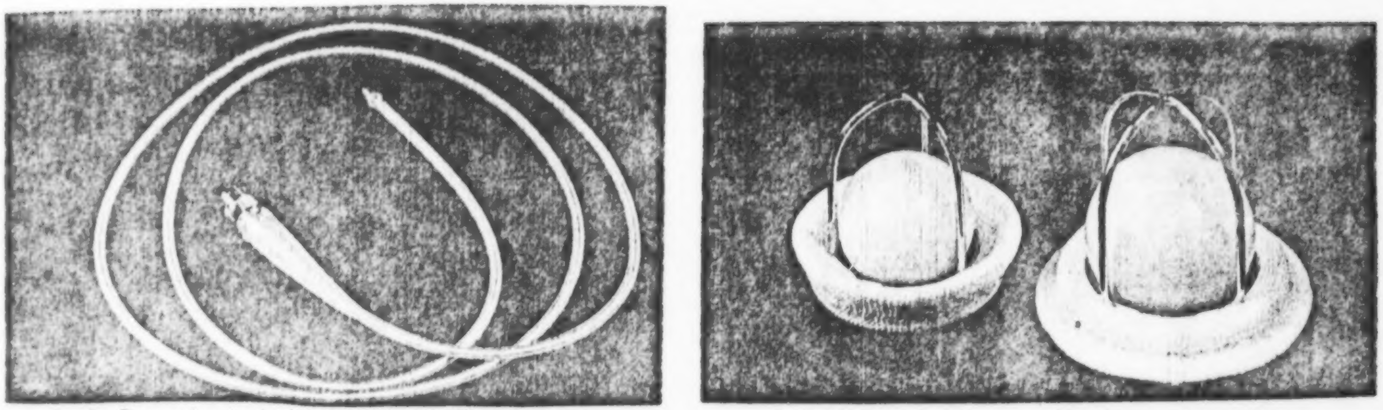


C. Latex rubber surgeons gloves and natural rubber plunger tip for syringe



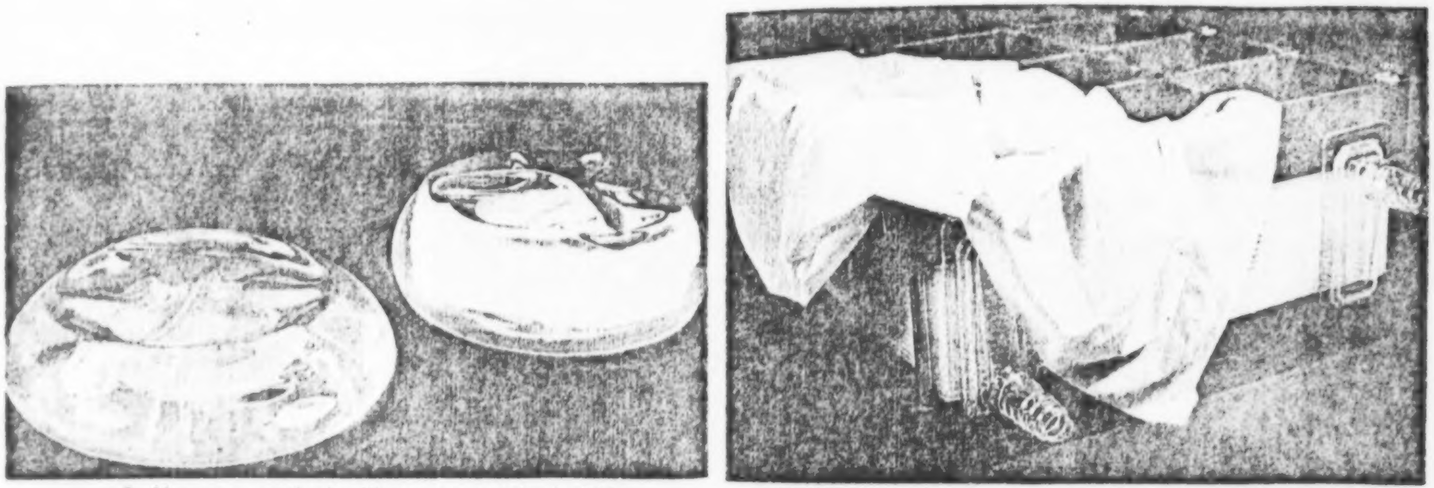
D. Latex rubber balloons for catheter tips

Figure 1. Medical products using natural or latex rubber.



A. Pacemaker lead wire covered with silicone rubber

B. Ball in cage heart valves with silicone rubber balls



C. Mammary prothesis, silicone get contained within silicone rubber membrane

D. Membrane Oxygenator using thin silicone rubber membrane

Figure 2. Medical products using silicone rubber.

The most common vulcanizing agent in natural rubber is sulfur used in concert with an activator such as zinc oxide. The accelerators and ultra-accelerators generally contain sulfur such as thiazoles, dithiocarbamates, thiurams, and mercaptans but also include aldehyde-amine condensation products. The fillers such as mineral clays, carbon blacks, silica, and metal oxides not only impart strength to the elastomer but can serve as a pigment to color the formulation. Antioxidants are usually amines and substituted or hindered phenols, and in our present-day society there is a need for antiozanants, which are phenylene diamines, quinoline derivatives, and waxes. If a foam is desired, then a blowing agent can be added, which decomposes during the heat cycle to liberate a gas which forms a cellular foam. These blowing agents can be azocarbonamides, hydrazine derivatives, or semicarbozide derivatives. Plasticizers and release agents can share some common agents such as stearic acid, petrolatum, paraffin, and finely powdered polymers.

The above components of rubber formulations are quite descriptive and do not require further comment regarding their applications or use.

Silicone Rubber

The formulations for silicone rubber could incorporate some of the components described above, but for medical applications most additives are generally avoided. The heat-vulcanized silicone elastomers used in medicine generally have three components; the gum, filler, and vulcanizing agent. The gum is usually a dimethyl polysiloxane containing less than 1-percent vinyl side groups which serve as free radical sinks. The filler, a fine particle fumed silica, is required if the elastomer is to have reasonable properties. The vulcanizing agent is a peroxide that decomposes during the curing operation to yield a free radical by which mechanism the crosslinking proceeds. The decomposition product of the vulcanizing agent is removed during a postvulcanizing heating cycle necessary for the elastomer to fully develop its properties. The final elastomer is then a two component system composed of the crosslinked dimethyl polysiloxane and silica filler.

Silicone elastomers used for other commercial applications such as food handling may also be utilized in the medical field. But, it is then incumbent on the manufacturer to apply more extensive chemical and biological testing methods to qualify such a material. Most manufacturers of products which utilize silicone elastomers are not the formulators of these compounds and have little control over the additives present when the basic polymer is formulated. These manufacturers may add components to the compound, but components already present in the formulation can only be removed with difficulty. Conversely, manufacturers using natural rubber in their products have a wide choice of components that can be incorporated into their formulations. These manufacturers also have the advantage of closer control of their formulations by either compounding the rubber inhouse or working in cooperation with a rubber compounder for a custom formulation.

Tables 1 through 3 show some typical formulations of natural and latex rubber using many of the classes of additives previously discussed. The formula in table 1 is typical for a bottle closure with self-sealing properties which must tolerate multiple penetrations with hypodermic needles for drug administration (ref. 2). This formulation with some modifications could also be utilized as a bottle stopper for I.V. solutions and plunger tips for syringes. Tables 2 and 3 are typical latex formulas for surgeons gloves and toy balloons respectively, both of which are dipped goods (ref. 3). Again, with some modifications these formula could also be utilized for the fabrication of prophylactics and the products shown in figure 1D. These products are balloon-tipped catheters utilized for removing blood clots from arteries and veins and also to float catheters into specific sites in the venous circulation. The formulation for these small balloons has relatively large amounts of antioxidants and antiozanants.

TOXICOLOGY

The toxicological requirements for elastomeric materials used in medical applications are significantly different and more stringent than those for other consumer elastomers. The elastomeric materials in medical applications are either in direct contact with tissue and blood or in

Table 1. Natural rubber formula typical for self-sealing puncture-resistant stopper (ref. 2)

Natural Rubber	100
ZnO	5
Platy Talcum	20 - 30
Calcined Kaolin	30 - 20
Tetramethylthiuram Disulfide	1.0
Mercaptobenzothiazole	0.5
Diethylene Glycol	2.0
Sulfur	1.25

Table 2. Latex rubber formula typical for surgeons gloves (ref. 3)

Natural Latex	100
KOH	0.4
Stabilizer (Sulfonate)	1.0
Wax Dispersion	0.5
Sulfur	1.25
Zinc Dibenzyldithiocarbamate	0.25
Zinc 2-Mercaptobenzothiazole	0.35
ZnO	0.75
Alkylated Bisphenol	1.0

Table 3. Latex rubber formula typical for toy balloons (ref. 3)

Natural Latex	100
Stabilizer (Sulfonate)	1.0
KOH	0.1
Alkylated Bisphenol	1.0
Sulfur	0.2
ZnO	0.2
Zinc Diethyldithiocarbamate	0.5

contact with a fluid to be placed in the blood stream or under the skin. The toxicology associated with most consumer elastomeric products is that concerned with general industrial safety and welfare. The industrial toxicity of elastomeric materials is most commonly associated with inhalation, ingestion, and/or skin contact with the potentially harmful agent; this is due to the usually large quantities of materials which are processed by the manufacturer. The toxicity in this instance would be directed toward the individual working in an environment with large quantities of chemicals.

The manufacturer of elastomers used in the medical field must face a different set of problems. The production worker generally does not face the same potential hazards as the quantities of materials handled at any one time are quite small, measured in grams, pounds, or kilograms. With medical elastomers it is the patient or the end user of the product who faces the potential hazard associated with the material. As stated earlier, most medical products come in contact with the end user either directly or indirectly. Blood and tissue fluids are potent solvents for extracting potentially toxic compounds from elastomers, particularly from natural and latex rubbers, due to their complex formulation.

The toxicology of components which enter into rubber formulations has been studied extensively in animals but is of limited value in the medical field. These studies have generally dealt with oral, contact, and/or inhalation toxicity of these materials and the responses are subject to numerous factors such as rate of absorption, dose administration, species, variation, alteration in gastrointestinal tract, solvent, etc. (refs. 4,5,6).

The National Formulary and the *U. S. Pharmacopeia* have specific biological tests which must be performed on rubber closures for injections and plastic containers (refs. 7,8). These tests are rather similar in nature and are outlined in table 4. The mouse and rabbit are the test animals used in these testing procedures and several different solvents are used to prepare extracts for testing. The extracts are prepared by mixing 20 ml of solvent with a sample having an equivalent surface area of 60 to 120 cm^2 and heating for 1 hour at 121°C. The extracts are then injected intravenously, intraperitoneally, or intracutaneously into the

Table 4. Toxicological testing scheduled for medical products

Test	Test Material	Animal	Number of Animals	Dose	Route of Administration*
I	Extract of Sample in Sodium Chloride Injection	Mouse Rabbit	5 2	50 ml/Kg 0.2 ml/animal in 10 sites	I.V. or I.P. I.C.
II	Extract of Sample in 5% Ethanol in Sodium Chloride Injection	Mouse Rabbit	5 2	50 ml/Kg 0.2 ml/animal in 10 sites	I.V. or I.P. I.C.
III	Extract of Sample in Polyethylene Glycol 400	Mouse Rabbit	5 2	10 gm/Kg 0.2 ml/animal in 10 sites	I.P. I.C.
IV	Extract of Sample in Sesame or Cottonseed Oil	Mouse Rabbit	5 2	50 ml/Kg 0.2 ml/animal in 10 sites	I.P. I.C.
V	Implant Strips of Sample	Rabbit	2	4 strips per animal	I.M.

*I.V. = Intravenous
I.P. = Intraperitoneal
I.C. = Intracutaneous
I.M. = Intramuscular

animals and the animals are observed for 3 to 7 days and compared to blank or negative control samples. In another test the material is implanted into the back muscle of rabbits and the implant site compared to a negative control after 3 to 7 days. These testing procedures are commonly utilized in the testing of medical elastomers and are reasonably good indicators of their biocompatibility.

Another set of tests commonly performed determine the compatibility a material will have with blood as measured by its effect on blood clotting and red blood cell damage. Briefly, extracts of the material prepared in sodium chloride injection are mixed with blood and allowed to incubate for 1 to 2 hours. The red blood cells are separated by centrifugation and if any damage has occurred, hemoglobin within the red cells will be released into the supernatant solution. The amount of hemoglobin released can be measured to indicate the extent of red cell damage. When blood is removed from the body it will clot in a short period of time, usually within 5 minutes. This factor is utilized in evaluating materials. Again, extracts of the material are mixed with blood and the time required for clot formation to occur is determined. An acceleration of the clotting would be quite harmful whereas a slight increase in the clotting time would be of little consequence and may in fact be advantageous.

Natural rubber formulations similar to that shown in figure 1 have been subjected to Test 1 and Test V of table 4 prior to vulcanization and after vulcanization on several occasions. The results of this testing indicated that prior to vulcanization this formulation exhibited a toxic response whereas after vulcanization a toxic response was not apparent. In those cases where the rubber was tested prior to vulcanization there was some necrosis and tissue hypersensitivity in the rabbit I.M. test and some of the mice in the test elicited a mild response, but there were no deaths in the series. No attempt was made to identify the causative agent or agents but it was apparent that a toxic material was extractable. Whether this toxic material was formed as a result of the extraction procedure or was extracted unchanged is not known. After vulcanization there was apparently no extractable toxic material. This could be due to the material having undergone an alteration to render it nontoxic, or the material could have become trapped in an insoluble matrix thereby being unextractable.

A precured latex dipping compound similar to that in table 3 has been subjected to Test 1 outlined above as well as to blood compatibility testing. This formulation was subjected to biological testing only in vulcanized form. The results indicated that no materials were extractable which would elicit a toxic response in the animal system or in the blood compatibility test, although a relatively large amount of material, up to 25,000 ppm, was extractable.

The complexity of the natural and latex rubber formulas can be sharply contrasted with the simplicity of the silicone rubber formulations. The number and type of additives which can be incorporated into silicone rubber is limited and includes fillers, pigments, heat stabilizers, blowing agents, plasticizers, and vulcanizing agents. In medical applications these additives are generally not utilized and the resultant functional elastomer is a two-component system composed of the crosslinked dimethyl polysiloxane and filler. The vulcanizing agent decomposes during the curing process and is almost entirely lost on postcure. In certain applications barium sulfate is added to the silicone rubber as a radio-opaque agent to allow the material to visualized by X-rays.

The vulcanizing agent in heat-cured silicone rubber is a peroxide, generally 2,4-dichlorobenzoyl peroxide, which decomposes during the curing to 2,4-dichlorobenzoic acid. The acid is driven off during the postvulcanization heat treatment. The acid present in postvulcanized silicone rubber can be extracted with organic solvent such as chloroform and very small quantities can be detected using gas chromatographic techniques. Generally less than 100 ppm of the acid can be found in postvulcanized silicone rubber samples. The acid has been subjected to biological testing using the intraperitoneal test in mice and intracutaneous test in rabbits at concentrations of 500, 1,000, and 1,500 ppm. It was found that the solvent caused a slight reaction in both tests. The material at a dose of 500 ppm gave essentially the same response as the control in both tests; at 1,000 ppm the response in the mouse I.P. test was slightly more severe than the control and was the same as the control in the rabbit I.C. test. At 1,500 ppm the response was definitely more severe than the controls. These results indicate that somewhere between 500 and 1,000 ppm 2,4-dichlorobenzoic acid will possibly start to elicit a toxic response. Whether this would also be true in man is unknown.

These are several factors which must be considered whenever results of animal testing are to be interpreted. One, there are vast species to species differences and the response in one species will not always be paralleled or mimicked in another species. Therefore, care must be exercised in transferring or correlating data between species. Two, the extracts which are prepared or the compounds to be tested are administered in a concentrated form. These components in actual practice would in most instances be leached from the material rather slowly; therefore, the total amount or dose would be spread over a prolonged period of time and would not elicit a toxic response. Three, the anatomical site where the material would be utilized would play a major role in the toxic effects. Some sites, such as the skin, are relatively insensitive and can tolerate a reasonable amount of insult, whereas other sites such as the bloodstream, are extremely sensitive and will not tolerate the slightest inbalance.

A desirable situation in regard to toxicological evaluation of material in animals would be to utilize the material in its functional form at the intended anatomical site. This is not always possible or feasible, particularly with the type of animals which have been under discussion. These animals are quite small and it would be difficult to implant a heart valve, insert a urethral catheter, or test a pacemaker in such animals because of their size and also their physiology, i.e., heart rates in excess of 150 beats per minute. In these instances larger animals such as dogs, sheep, calves, and pigs are generally utilized.

SILICONE RUBBER FAILURE

As mentioned earlier, the effect of the biological environment on materials is just as important as the converse when these materials are used in medical devices. Silicone rubber was used successfully for many years in contact with the blood stream as shunts to drain excess fluids from the cranium of hydrocephalic patients (ref. 1).

With the development of heart valves in the early 1960's, this material was selected as one with proven biocompatibility and which could prove useful as a poppet. Several years after its introduction as a ball in a heart valve prosthesis, similar to that shown in figure 2B, it was reported the valve failed due to the ball escaping from the cage (ref. 9).

Shortly thereafter, several reports of failure of silicone rubber in this application were also reported. The cause of the failure of silicone rubber was soon found to be due to lipids being absorbed into the silicone rubber (ref. 10). Lipids are not found free in the blood stream but are transported as micellar lipoprotein complexes. Lipids have been the only type of compounds isolated and identified from failed silicone rubber except for a recent report which cites evidence for the presence of free amino acids (ref. 11). The amount of lipids extractable from a failed silicone ball varies from 3 to 40 percent with an average of approximately 18 percent (ref. 12). The sequence of events which occurs to cause failure is not known but lipid absorption appears to be prerequisite to ball variance. It would be reasonable to assume lipids enter the silicone rubber ball and as the concentraction increases, the ball begins to swell and lose its physical properties such as tensile, elongation, and abrasion resistance. The swelling and loss of physical properties can cause events such as sticking in the cage, abrading of the silicone polymer, and/or crack formation and propagation to occur either singly or in concert.

As the variant ball is returned to the laboratory the weight and dimensions of the ball can be increased or decreased when compared to an unimplanted ball. The variant ball is typically found to have acquired a yellow creamy color, and is no longer spherical or translucent. The surface shows significant damage, has lost its smooth, shiny appearance, and may no longer be continuous. Examples of the types of variant balls which are encountered are shown in figure 3 with an unused ball for comparison.

A great deal of effort has been expended in attempting to determine the cause of failure of silicone rubber when used in prosthetic heart valves. An artificial system whereby lipids similar to those found in the blood stream can be introduced into silicone rubber has been developed (ref. 13). The amount of lipid absorbed by the silicone rubber is a function of the exposure time and levels off at approximately 2 percent

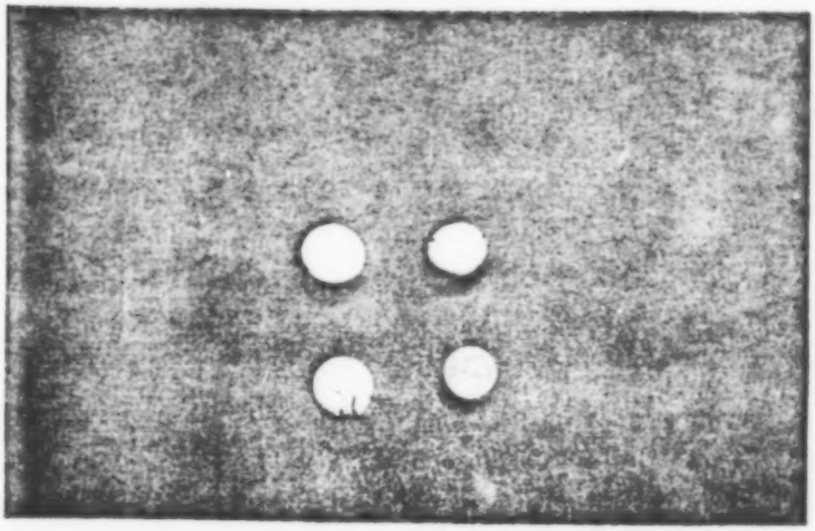


Figure 3. Silicone rubber balls used in heart valve prostheses, lower right, new silicone rubber ball, remainder implanted variant silicone rubber balls.

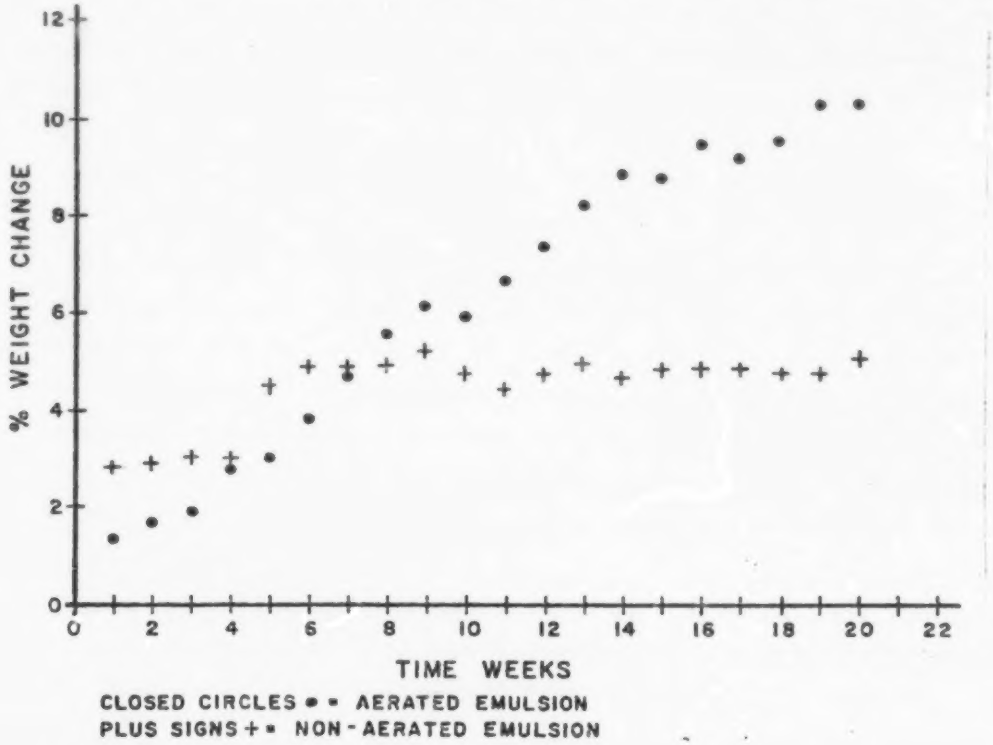


Figure 4. Weight gain in silicone rubber after exposure to unsaturated fatty acids.

in 90 days. This small amount of lipid is insufficient to cause the same type of variance as noted clinically. The same authors have also presented evidence showing that oxidation products of lipids accumulate in silicone rubber and may be the cause of the increase in weight (ref. 14). Linoleic acid used as the model compound, was artificially introduced into silicone rubber balls by swelling and then subjected to 100-percent oxygen for 120 days. After this time the silicone balls assumed a physical appearance similar to a variant ball. The organic solvent extracts of the in vivo variant ball showed the same type of oxidized polar compounds as that observed with an in vivo variant, as determined by thin layer chromatography, infared spectroscopy, nuclear magnetic resonance, and mass spectroscopy.

A simple in vivo system was set up in attempts to duplicate the type of weight increase and variance noted with clinical samples. A 4-percent aqueous emulsion of unsaturated fatty acids was aerated by pulling air through a gas washing bottle. Silicone balls were placed in this environment and weighed periodically. The media was changed approximately twice weekly. In 20 weeks the weight gain of the silicone balls had exceeded 10 percent and the samples had assumed a yellowish color. The percent weight change as compared to a silicone rubber ball in an unaerated emulsion is shown in figure 4. Aeration caused a twofold increase in the weight uptake in a reasonably short period of time. Thus, there are presently two methods for duplicating silicone ball variance to study and attempt to understand the mechanism of this phenomenon.

Several years ago a theory was postulated to explain the phenomenon of ball variance (ref. 15). The theory proposed that lipids carried in the blood stream as lipoprotein complexes were degraded due to the capacity of the environment in the vicinity of the valve to liberate free lipids. The transient high concentration of free lipids in the vicinity of the valve allowed the silicone rubber to absorb these lipids. This theory taken with the observations of Carmen and Mutha becomes more feasible because lipid oxidation could proceed in the presence of the high oxygen content (Po_2 = 110 mmg Hg) present in the arterial system (ref. 14). This theory has not been proven but evidence to support it is being accumulated in several laboratories.

The failure of silicone rubber as a heart valve poppet has been reported to occur with an early model valve used for aortic valve replacement. This particular model of valve was used approximately 4 years and there have been 250 reported instances of ball variance for an overall incidence of less than 2 percent. This valve was redesigned approximately 9 years ago and since that time there has been a total of eight variant silicone rubber balls from this prosthesis for an incidence of approximately 0.04 percent. Whether or not silicone rubber variance in heart valves has been resolved by the valve design change cannot be stated with certainty. The statement which can be made with a fair degree of confidence is that the incidence of silicone rubber failure in this model of heart valve has been significantly delayed.

Silicone rubber variance is unique to humans as it has never been demonstrated in experimental animals. This is an excellent example of two of the precautions previously discussed regarding the species differences and evaluation of a material in its intended form at the proper anatomic site.

SUMMARY

A brief review of some of the elastomers used in the medical field along with a few of their applications was presented. The requirement for sophisticated toxicological testing and some test methods used to evaluate elastomers in the medical field were discussed. An indepth view of the failure of silicone rubber as an occluder in heart valve prosthesis was presented.

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DISCUSSION

MR. SUNDAR L. AGGARWAL: (The General Tire and Rubber Company, Akron, Ohio): Of course, the silicone rubbers are rather comparatively older elastomers. Recently, there have been many developments in elastomers, particularly in the area of plastic elastomers, which require no external cloth sticking. Now, I wonder if there is any effort that you know of where the new developments in elastomers are being evaluated?

DR. KOORAJIAN: Yes, I am personally unaware of the system that you are talking about. We are looking at another type of silicone rubber. I did get into this, but we did develop a method for artifically inducing a ball variance, and we utilized this method to test various materials. We are presently looking at a fluorosone rubber which behaved very, very well in our vitro system. At present it is undergoing in vivo evaluation in a dog. If this proves successful, we will probably use a very limited number in clinical applications to see how it goes. This is a very difficult question--silicone rubber, after about 9 years now, has behaved very well in our new model valve. We are reasonably hesitant to change a material right now, because it would take a long time to qualify that material, because silicone is behaving very well. I can't emphasize that it is to date. The stuff might fall apart next year. We just don't know, but it takes a long time to qualify material for these applications.

THE IDENTIFICATION OF EFFLUENTS FROM RUBBER VULCANIZATION*

Stephen M. Rappaport, Ph.D.†

Abstract

From the viewpoint of occupational health, the vulcanization of rubber presents an unknown factor. Since exposures are poorly defined, toxic responses are difficult to predict on the basis of either acute or chronic effects. Likewise, the few published mortality and morbidity studies indicate only possible problems, notably carcinogenesis.

This investigation supplies qualitative and quantitative analysis of the C_6 - C_{25} *organic fraction discharged from an actual rubber stock during cure. Initially, vapors are generated and collected in the laboratory whereupon the combined techniques of gas chromatography and mass spectrometry are used to separate and to identify individual compounds. Then, environmental sampling and analysis establish the airborne concentrations of these substances in the manufacturing area.*

Identified in the vulcanization effluent is an unusual assortment of compounds, including styrene, butadiene oligomers, alkyl benzenes and naphthalenes, and several nitrogen and sulfur-containing substances. Most of these are traced to individual formulation ingredients, i.e., the polymers, an aromatic oil, the antiozonant, and the accelerator. Air concentrations for compounds confirmed in the curing area (a passenger tire press room) range from a high of 1.5 ppm to 5 ppb and vary inversely with boiling point; thus, the more abundant substances are in the C_6 *to* C_8 *boiling range.*

When considering rubber processing operations from an occupational health viewpoint, the vulcanization stage represents an unknown factor. During this phase, rubber stocks (formulations of technical compounding ingredients) are subjected to high temperatures and a barrage of chemical reactions designed to transform them into finished products. Concurrently, a mixture of organic vapors is introduced into the workplace. Since the identities and exposure concentrations of these substances are unknown, process evaluation is impossible.

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*This study was submitted as a doctoral dissertation to the Graduate School of the University of North Carolina at Chapel Hill. The work was performed in the Department of Environmental Sciences and Engineering in association with the Occupational Health Study Group.

†Los Alamos Scientific Laboratories, Los Alamos, New Mexico 87544.

Epidemiological data concerning the relative health of vulcanization personnel is inconclusive. What information is available gives the impression that a problem might exist, especially carcinogenesis. Unfortunately, most published epidemiological studies of the rubber industry did not break down the general population according to job category.

Investigations which did provide classification of curing personnel gave mixed results. Parkes in Great Britain showed no unusual findings as the result of absenteeism records of vulcanization workers in the rubber and cablemaking industries of that country between 1958 and 1959 (ref. 1). In an investigation of a small U.S. rubber company (producing passenger tires), Mancuso et al. revealed that curing workers did have consistently higher mortality rates than most other departmental groups, especially from two causes: malignant neoplasms and diseases of the circulatory system (ref. 2). The small sample size (91 total deaths of 655 persons in the "curing and tire building" department) of this 1940-1964 cohort study negated meaningful observation, however. Cancer was also found to be consistently more prevalent among vulcanization workers in a recent cohort of 40,867 subjects employed in Britain's rubber and cablemaking industries as reported by Fox et al. (ref. 3). The most significant finding was a consistently higher age standardized mortality rate for these individuals from bronchial cancer ($P<.05$), although again the small number of reported cases (15) rendered conclusions tenuous.

A review of toxicology literature also provides little information concerning the health significance of vulcanization effluents. This stems primarily from the fact that the extent of discharges of specific additives (for which there is toxicological data) is unclear. If certain compounding ingredients are released intact and in sufficient quantity, systemic health effects might be suspected (refs. 4-13). Likewise, since several classes of formulation additives have been associated with carcinogenesis (e.g., aromatic amines and nitrosamines used as antidegradants and retarders, respectively), the release of these substances could also be significant (refs. 14-29).

Without concrete analytical data, however, any prediction of toxicological significance is highly speculative. Bourne et al. commented on this paucity of information and specifically recommended that fumes from curing moulds be investigated (ref. 13).

Thus, there are several questions pertaining to vulcanization processes that must be answered to establish their health implications. Which compounds are released from a stock during cure, and where do they originate? This two-part question identifies the importance of determining not only which volatiles are driven from a specific processing unit but also their origins within that unit. Thus, losses may be classified (i.e., volatilized additives, impurities of additives, reaction products), and conclusions based upon analysis of a particular stock may be generalized to other stocks and processes. What are the concentrations of these substances within the curing room? Obviously, the coupling of qualitative and quantitative data precedes any meaningful evaluation. Do these exposures present a hazard to vulcanization personnel? This, the most important question, is also the most difficult to answer. An answer presupposes that sufficient information concerning acute and chronic health effects of known or suspected substances is available. Unfortunately, this is rarely the case, especially regarding carcinogenesis, which is little understood.

EXPERIMENTAL

The purpose of this investigation was to determine exposure concentrations of organic compounds released from a rubber stock during cure. Toward this end, qualitative analysis identified individual substances, and quantitative methods provided actual exposure levels.

The investigation was divided into several sections. First, methods were developed for generating vulcanization effluents from an actual "green" stock within the laboratory and for collecting the organic fraction. Then, gas chromatographic techniques were coupled with mass spectrometry to separate individual compounds from the mixture, to associate them with those discharged from individual rubber additives, and to identify them. Finally, field air samples were collected in the manufacturing area, and the presence of several previously identified compounds was confirmed.

The stock selected for study was the tread portion of a bias-ply passenger tire produced by a large rubber manufacturer. It represents a common stock of typical formulation cured in high volume by all major rubber companies. Furthermore, due to the nature of the curing process and of the exposed tire surface, it was anticipated that this stock would contribute a significant portion of the airborne materials released. The formulation for this stock is given in table 1. It was prepared with bench scale processing equipment, slabs being milled to a thickness of 1/4 in.

Table 1. Formulation of tread stock from a bias-ply passenger tire use in this investigation

Ingredient	Percent by weight (approximate)
Polymer	
Styrene-butadiene rubber (1)	25
Styrene-butadiene rubber (2)	25
Polybutadiene rubber (cis)	10
Antidegradant[a]	
N-phenyl-N-*sec*.butyl-p-phenylenediamine	0.5
Accelerator[b]	
N-*t*.butyl-2-benzothiazole sulfenamide	0.5
Diphenyl guanidine	0.1
Oil	
Aromatic (total[c])	20
Carbon black	
Furnace black	30
Miscellaneous	
Sulfur	0.5
Activated zinc oxide	0.5
Stearic acid	0.5
Sunproof wax	0.5

[a] N-phenyl-N'-*sec*.butyl-p-phenylenediamine = Flexzone 5L.

[b] N-*t*.butyl-2-benzothiazole sulfenamide = Santocure NS.

[c] Since some oil is used to extend the SBR's, the figure shown here is the total weight percent for all oils; this brings the total to greater than 100 percent.

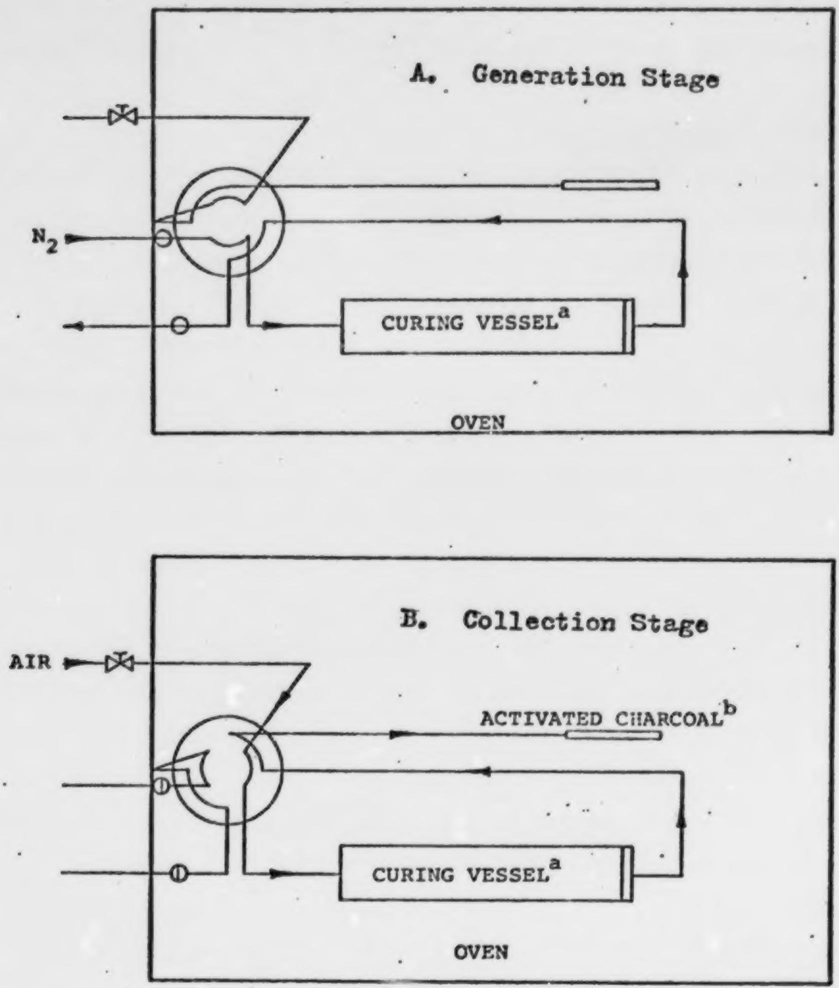
and stored in 1 ft x 1 ft sections until ready for use. Portions of all compounding ingredients were also stored for use in correlation experiments.

Generation and Collection of Volatiles

After considering important vulcanization parameters to be reproduced (temperature/duration, reducing environment) and reviewing several papers which described the heating of polymers within inert environments (refs. 30-35), the following generation technique was selected. A 50 gm piece of uncured rubber was placed in a stainless steel curing vessel, which was purged with nitrogen and sealed with toggle valves (figure 1-A). Free of air, the vessel was heated in an oven to simulate the actual tire press closing and vulcanization stages. As the stock cured over a 20-minute period, volatiles were released from it and retained in the closed system.

Following the curing stage the vessel was slowly cooled and was concurrently purged with air to wash the effluent into a collection device downstream (fig. 1-B). Adsorption on activated charcoal was selected for this purpose because of the high collection efficiency for organic compounds, the ease of solvent desorption (for the analysis stage which followed), and the insensitivity to water (refs. 36-44). This portion of the experimental cycle (analogous to the actual press opening and cooling stage) lasted approximately 30 minutes and effectively trapped the C_6 and greater organic fraction.

Prior to the separation and identification stages, a preliminary investigation determined the relationship between percent weight loss from the stock and temperature. This data was used to assess the reproducibility of the experimental cycle and to establish the level of emissions from the stock over the relevant temperature range. Fourteen randomized trials were conducted between 160 and 200°C at 10°C increments with a constant curing duration of 20 minutes. Figure 2 shows the first order regression of percent weight loss on temperature, which was significant ($P<.001$) with no significant lack of fit ($.10<P<.25$). These results showed the generation procedure to be reproducible with gross volatilization from the stock varying linearly between 0.19 and 0.27 percent by weight. Remaining experiments utilized the normal curing temperature of 180°C, a value in the middle of the tested range (20-minute curing duration).


A. Generation Stage
N2
CURING VESSEL[a]
OVEN
B. Collection Stage
AIR
ACTIVATED CHARCOAL[b]
CURING VESSEL[a]
OVEN

[a] Stainless steel pressure filtration funnel, 200 ml capacity (Gelman), with 47 mm high-efficiency glass fiber filter at outlet.

[b] Stainless steel tubing, 80 mm × 6.5 mm O.D. × 4 mm I.D., containing 200 mg of 80/100 mesh activated cocoanut charcoal (Fisher Scientific) held by silane-treated glass wool plugs.

Figure 1. Apparatus for generation and collection of volatiles from curing tread stock.

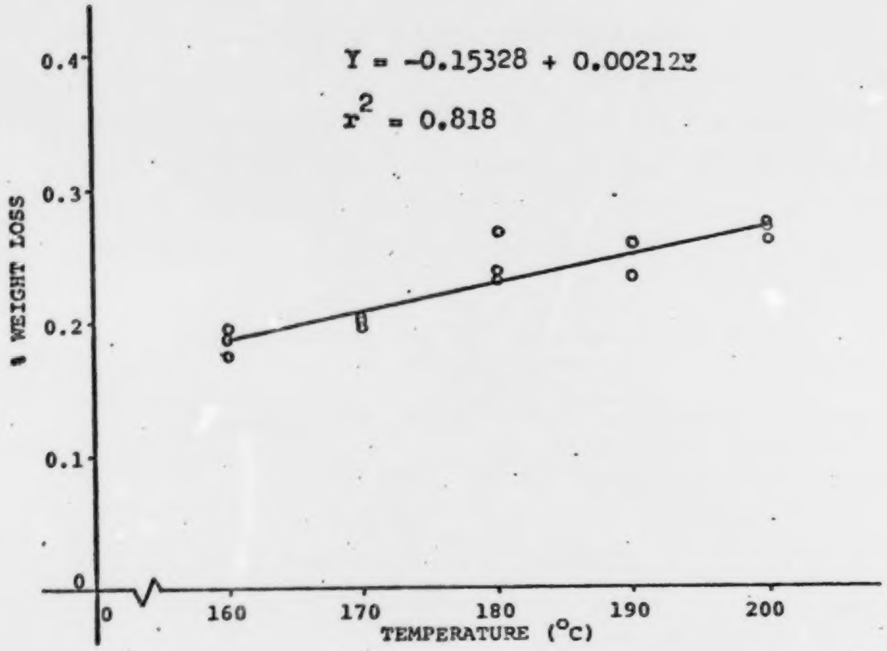


Figure 2. First order regression of percent weight loss on temperature of selected tread stock.

(Stock size of 50 gm, i.e., 2 pieces, each 6 in. × 1 in. × 1/4 in., heated for 20 min. in N_2 and cooled under continuous 70 ml/min air flow for 30 min to room temperature.)

Separation and Identification of Compounds

The materials adsorbed on the charcoal were eluted with 1.0 ml of ethyl ether using the apparatus and procedure shown in figure 3. This desorption method was tested with toluene (20 mg total adsorbate) and was reproducible, averaging 89.2 percent recovery for triplicate trials. Prior to gas chromatography the eluate was reduced in volume under dry nitrogen from 1.0 ml to 50-75 μl, thereby increasing the relative concentration of higher boiling compounds.

An aliquot of the eluate was injected into a gas chromatograph with experimental parameters given in table 2. The column contained a methylsilicone oil liquid phase to effect a boiling point separation and to allow temperature programming. It was prepared according to the procedures outlined by Dunham and Liebrand (ref. 45) and had an efficiency of 21,000 theoretical plates for n-nonane under isothermal 100 °C operation.

Figure 4 shows typical chromatograms for the curing volatiles (B) and a control (A) (obtained by carrying a charcoal tube through the procedure

Table 2. Parameters for gas chromatography

- Apparatus
  - Instrument: Perkin Elmer Model 990 Gas Chromatograph
  - Detector type: Flame ionization
  - Recorder range: 1 mV full scale
- Column
  - Length and diameter: 50 ft × 0.125 in. O.D. × 0.085 in. I.D. (2 × 25 ft sections joined with a Swagelok 1/8 in. stainless steel union)
  - Material: Stainless steel
  - Packing: 3.1 percent SP-2100 on 80/100 mesh Gas Chrom-Q
- Temperatures, °C
  - Injection port: 200
  - Detector: 200
  - Column: Temperature programmed from 50 to 160 at 2°/min and 160 to 330 at 6°/min
- Flow rates of gases
  - Carrier gas (He): 30 ml/min isorheic
  - Hydrogen: 35 ml/min
  - Air: 400 ml/min
- Sample
  - Volume: 3 μl
  - Retention times: Relative to styrene

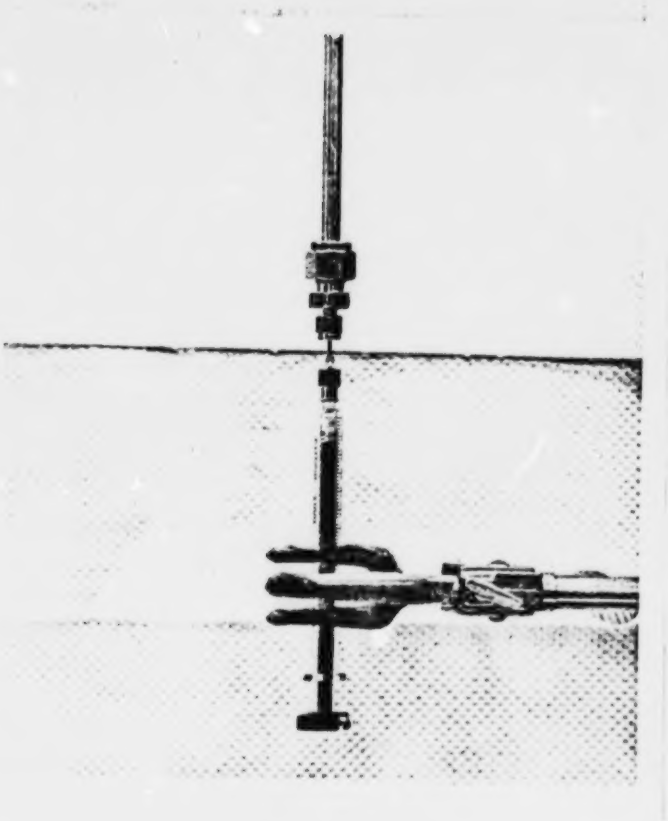
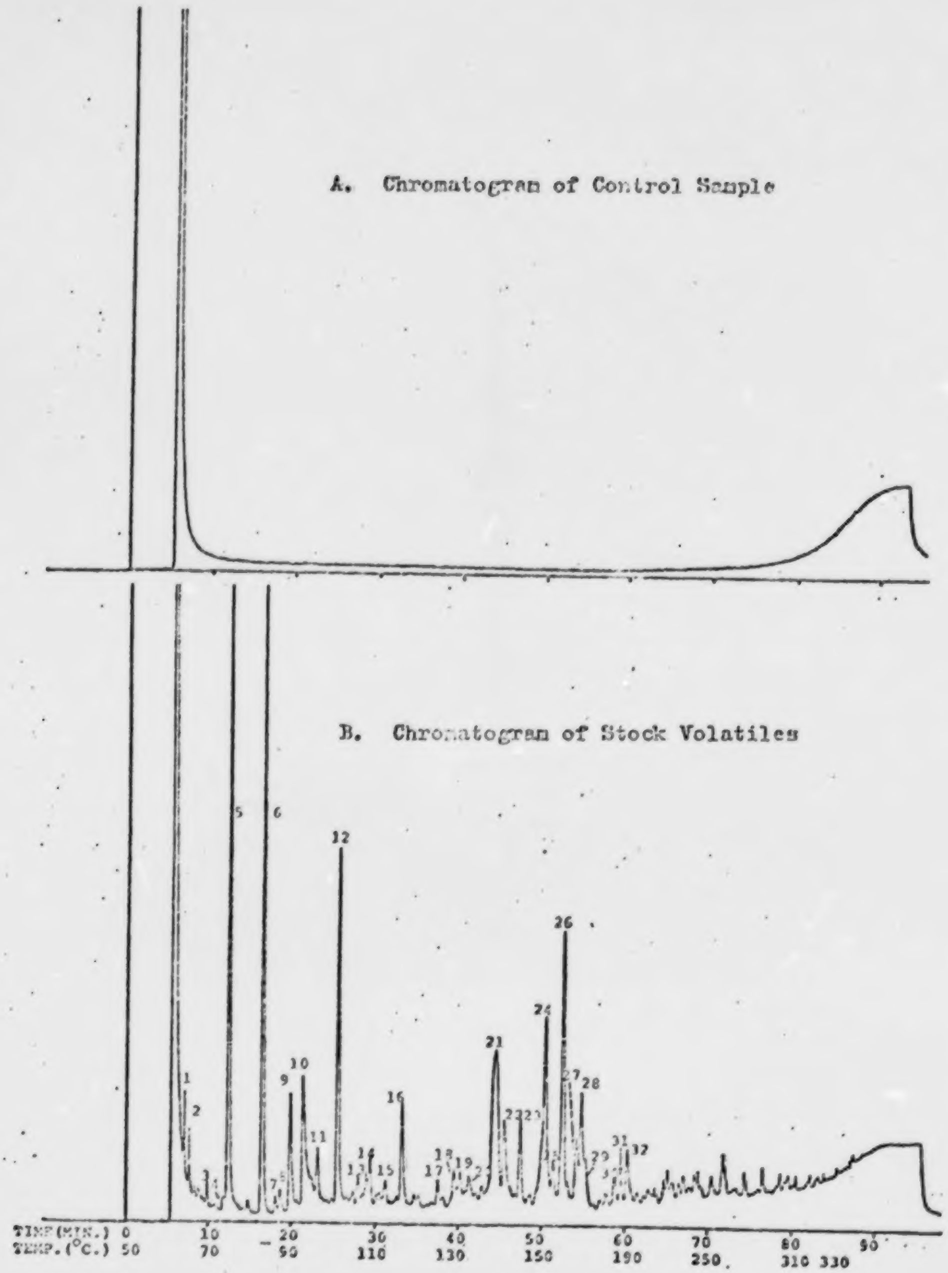


Figure 3. Apparatus for elution of adsorbed curing volatiles from activated charcoal.

(The charcoal tube was positioned with its inlet side down; 300 μl of diethyl ether were then drawn through the absorbent bed by withdrawing the gas-tight syringe a like volume. The tube was capped with Teflon tape and allowed to stand for 30 min, whereupon an additional 1.0 μl of diethyl ether was drawn through the tube and collected in the receiving syringe.)



A. Chromatogram of Control Sample

B. Chromatogram of Stock Volatiles

Figure 4. Gas chromatography of curing volatiles and a control sample (parameters given in table 2).

with no sample in the curing vessel). It reveals numerous peaks in the experimental sample not present in the control. Compounds are abundant throughout the temperature program with the major ones in the lower boiling region. Analysis of a series of n-alkanes (C_6-C_{25}) defined the approximate boiling range for these peaks to be between 80 and 250 °C (peaks 3 to 32).

In order to compare volatiles released from the stock with those discharged from specific rubber additives, each compounding ingredient was carried through the heating, collecting, and separation stages individually (using twice the amount contained within a 50-gm stock sample). A small amount of styrene was added to the extracts prior to injection into the gas chromatograph as an internal reference for determination of relative retention times. It was not added to the two styrene-butadiene rubber extracts since it was a natural component of them.

Figures 5 through 12 show the results of these experiments. In each case the chromatogram of the total effluent (B) is placed directly below that of the ingredient (A) for reference. Chromatograms of four ingredients (sulfur, zinc oxide, stearic acid, and sunproof wax) are not included since no significant peaks were resolved.

There is good correspondence between relative retention times of peaks from the ingredients and from the stock. Especially clear is the comparison with the cis-polybutadiene rubber (fig. 7) which shows major peaks matching quite closely. Other ingredients, including the styrene-butadiene rubbers, diphenyl guanidine, and the antiozonant, generated relatively few volatiles, but these, too, correlated well. The oil contributed a series of low abundance compounds, primarily in the higher boiling region, while the sulfenamide accelerator produced several large peaks, two of which matched those from the entire stock.

An aliquot of the stock volatiles eluate was subjected to combined gas chromatography-mass spectrometry under parameters listed in table 3. An identification was based upon the compound's mass spectrum and its gas chromatographic retention time or an estimate of its boiling point, depending upon the availability of an analytical standard.

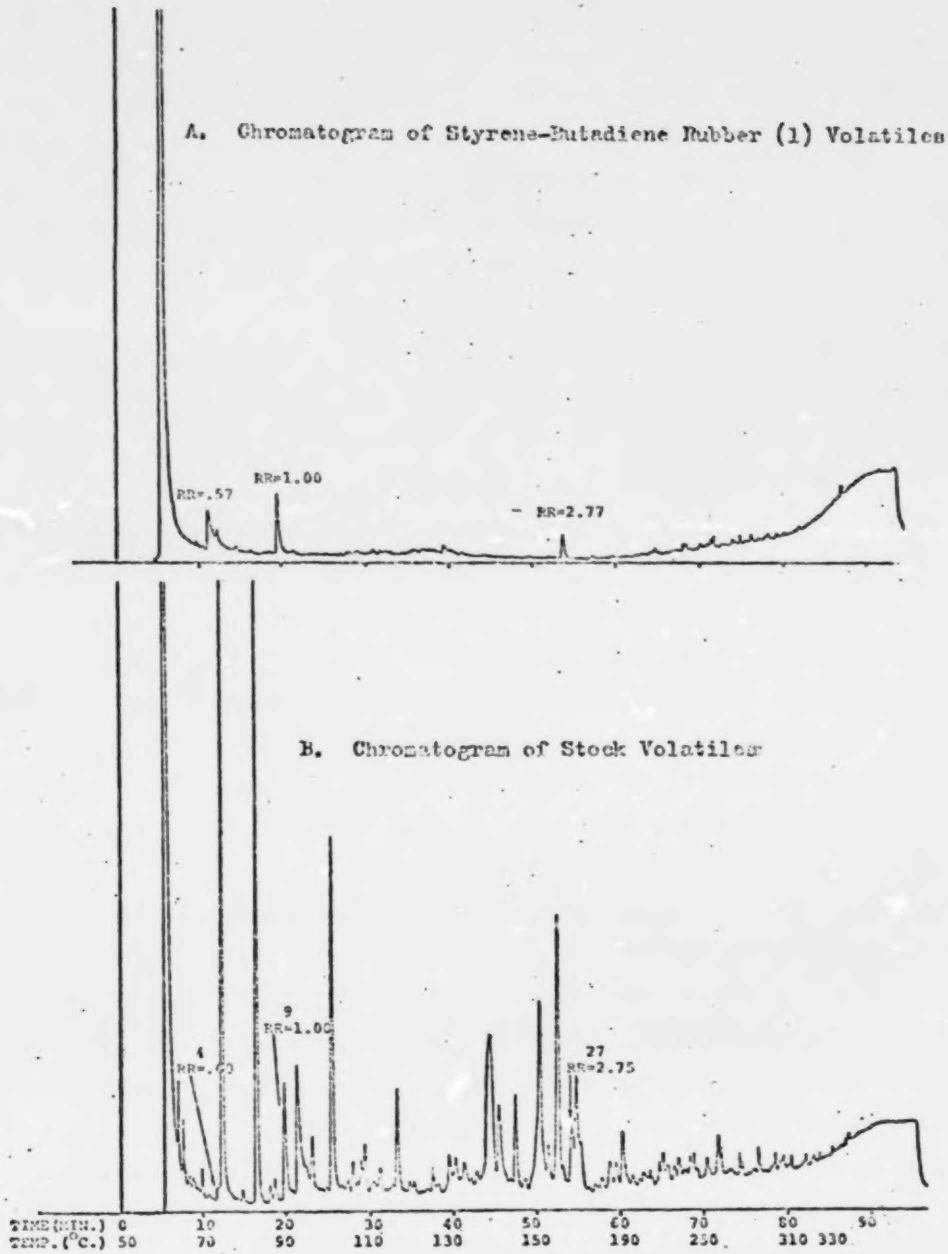
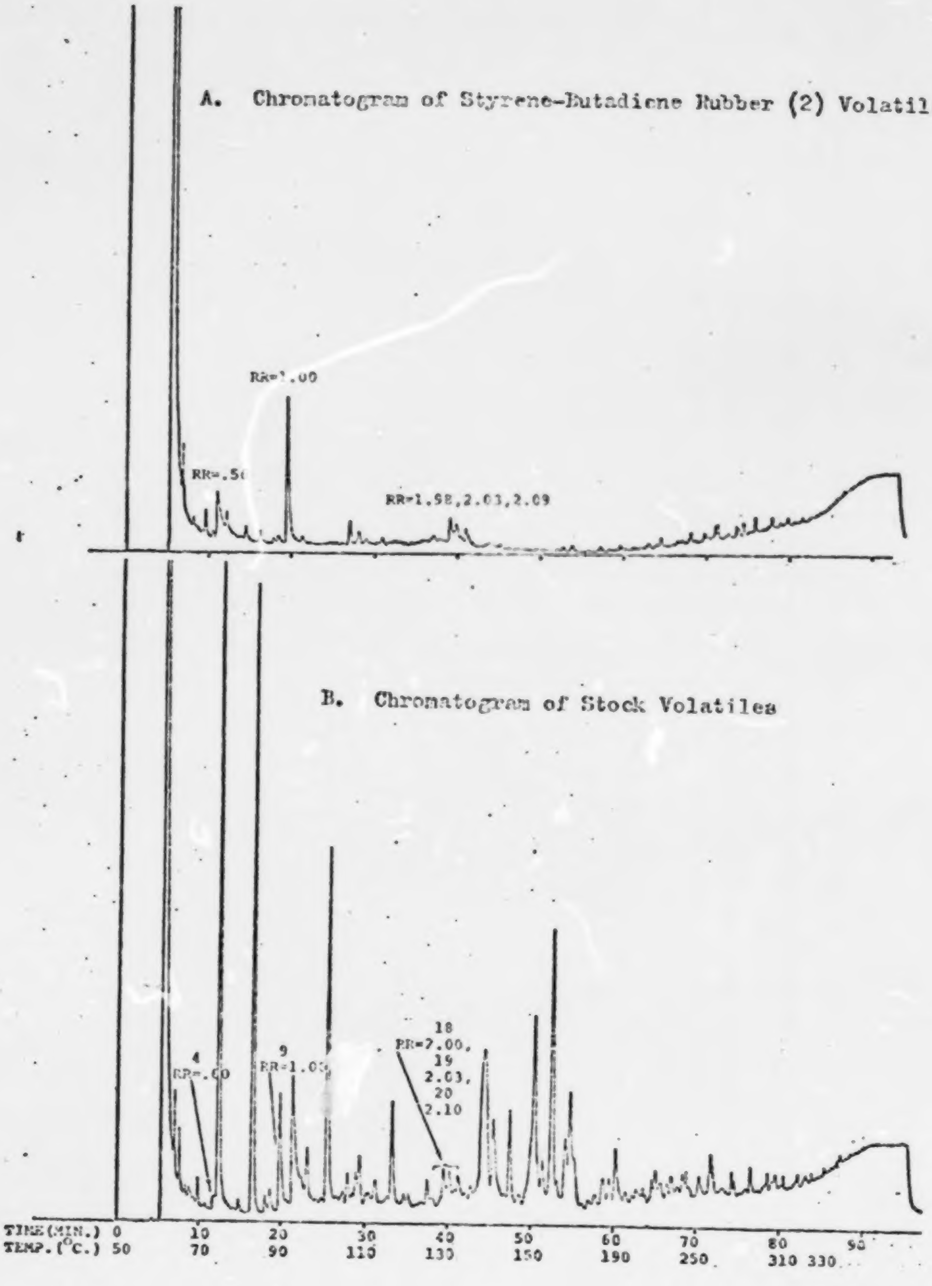


Figure 5. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).



A. Chromatogram of Styrene-Butadiene Rubber (2) Volatiles

B. Chromatogram of Stock Volatiles

Figure 6. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).

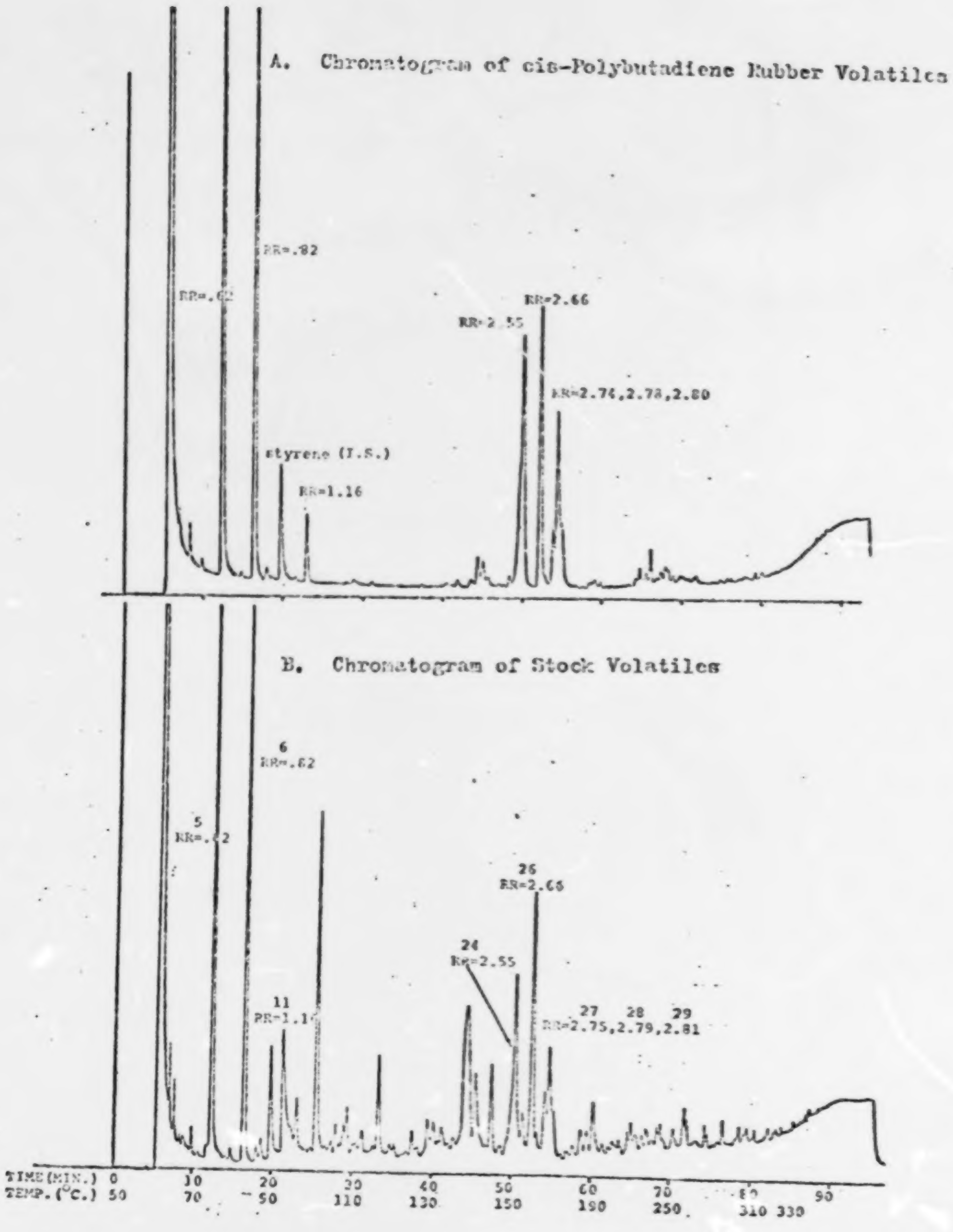


Figure 7. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).

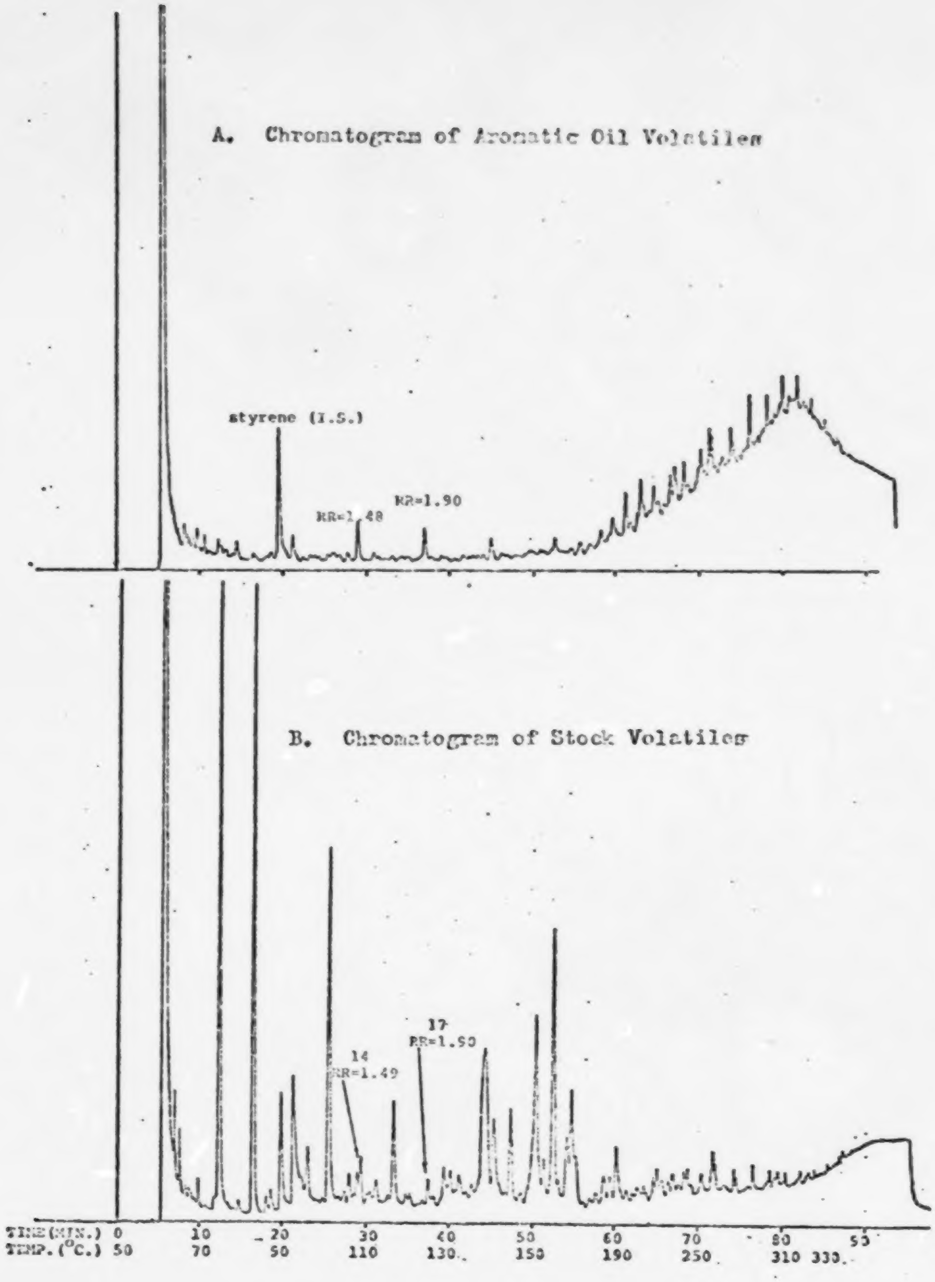


Figure 8. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).

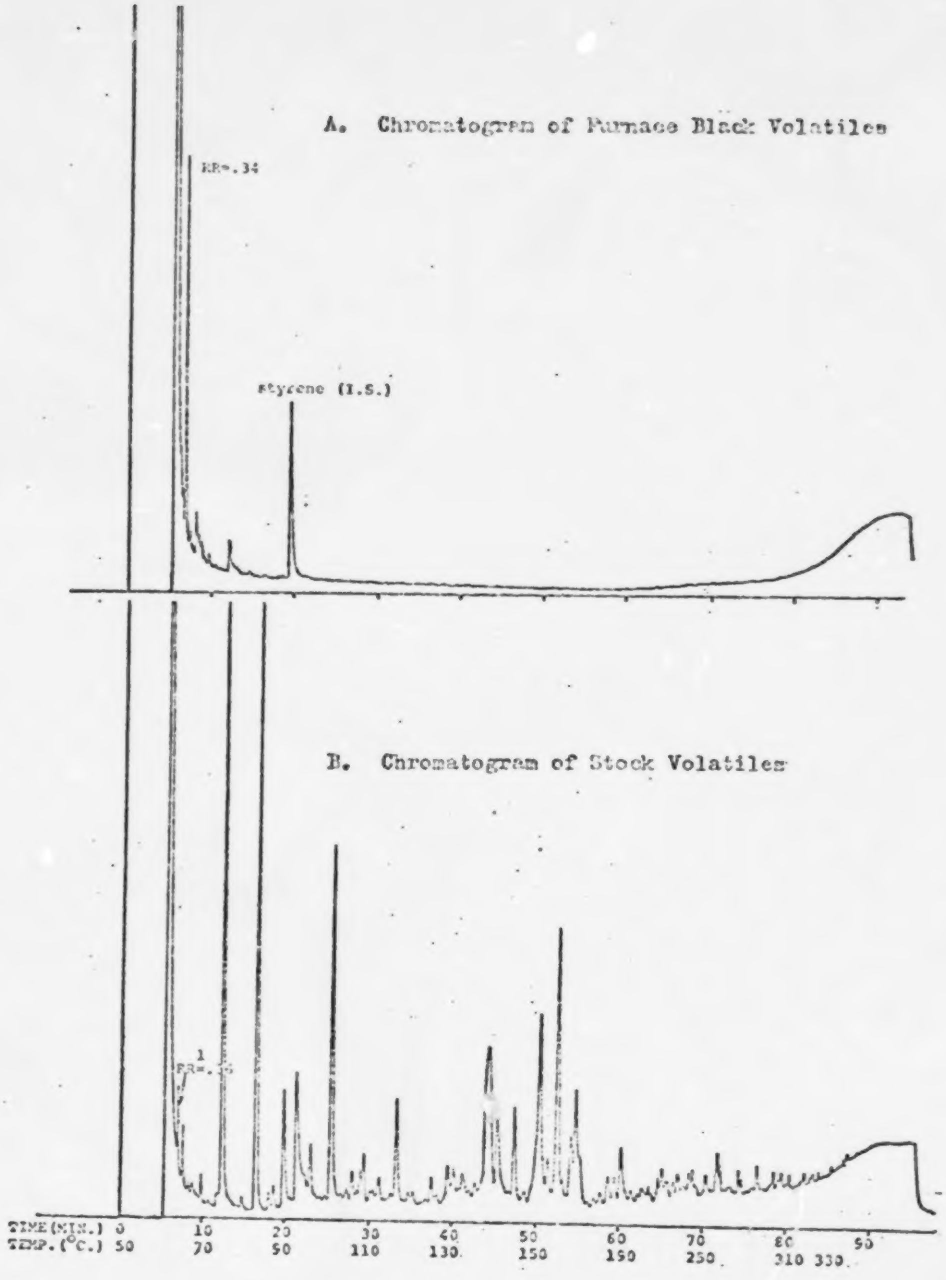
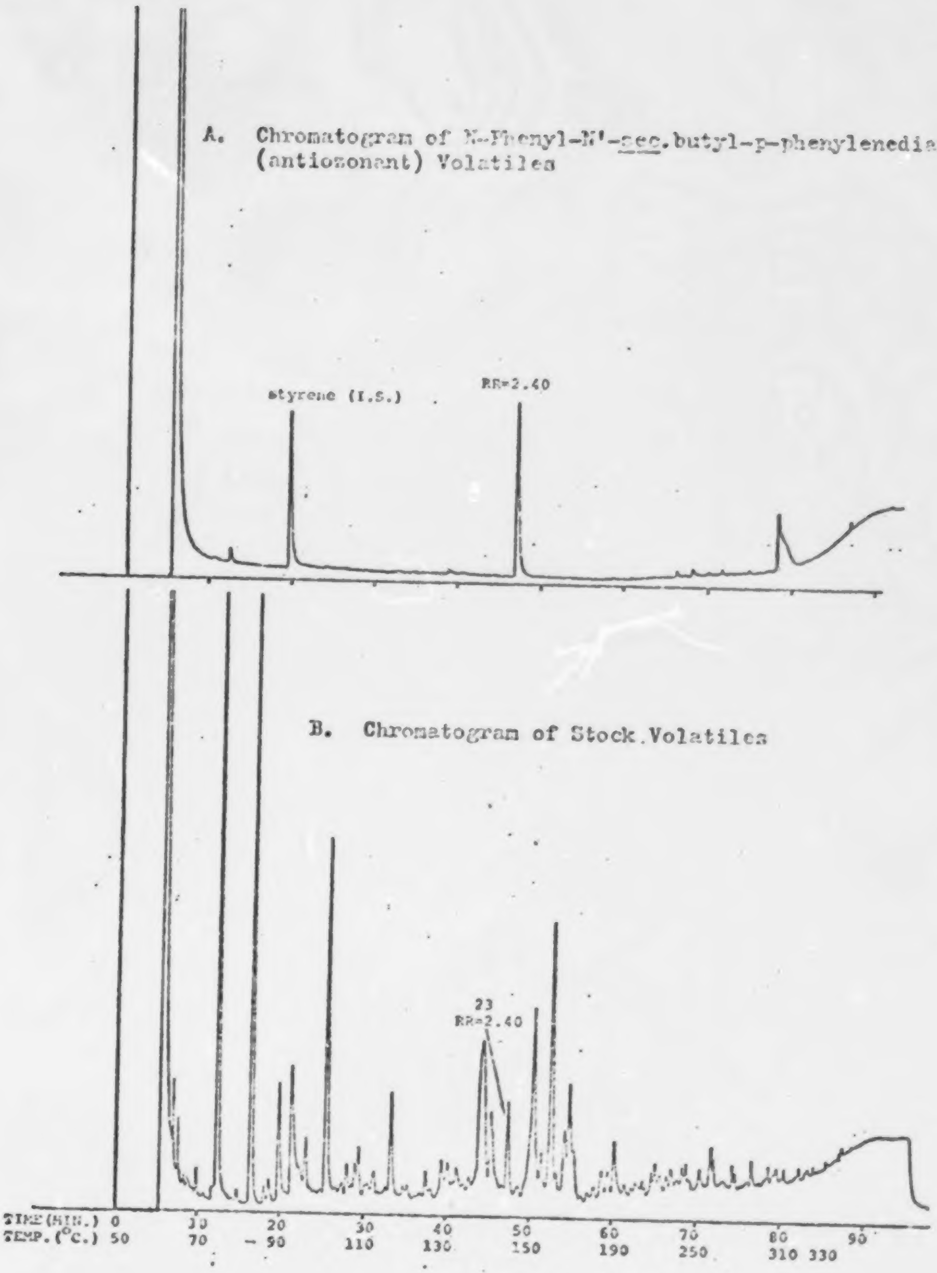


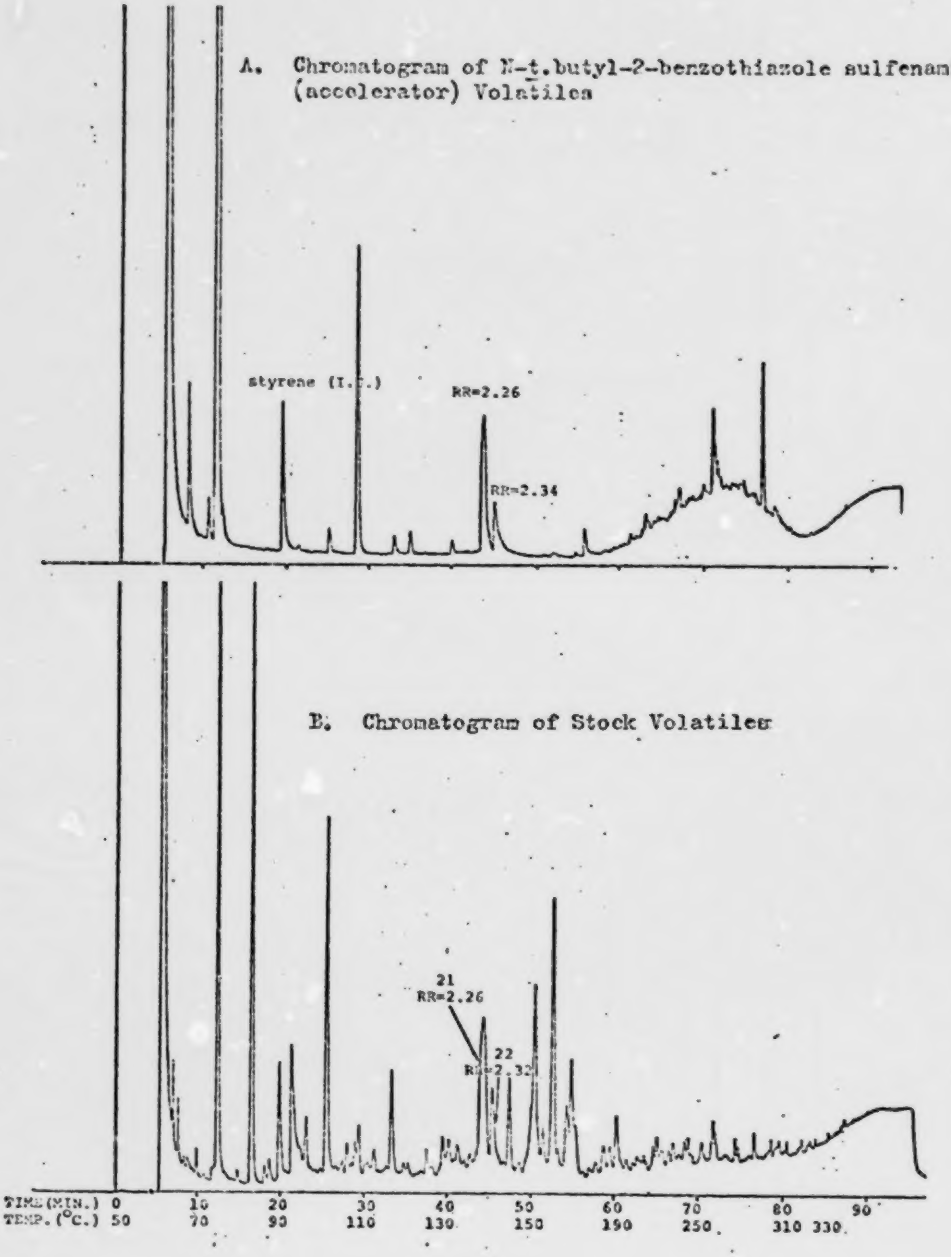
Figure 9. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).



A. Chromatogram of N-Phenyl-N'-*sec*.butyl-p-phenylenediamine (antiozonant) Volatiles

B. Chromatogram of Stock Volatiles

Figure 10. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).



A. Chromatogram of N-t.butyl-2-benzothiazole sulfenamide (accelerator) Volatiles

B. Chromatogram of Stock Volatiles

Figure 11. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).

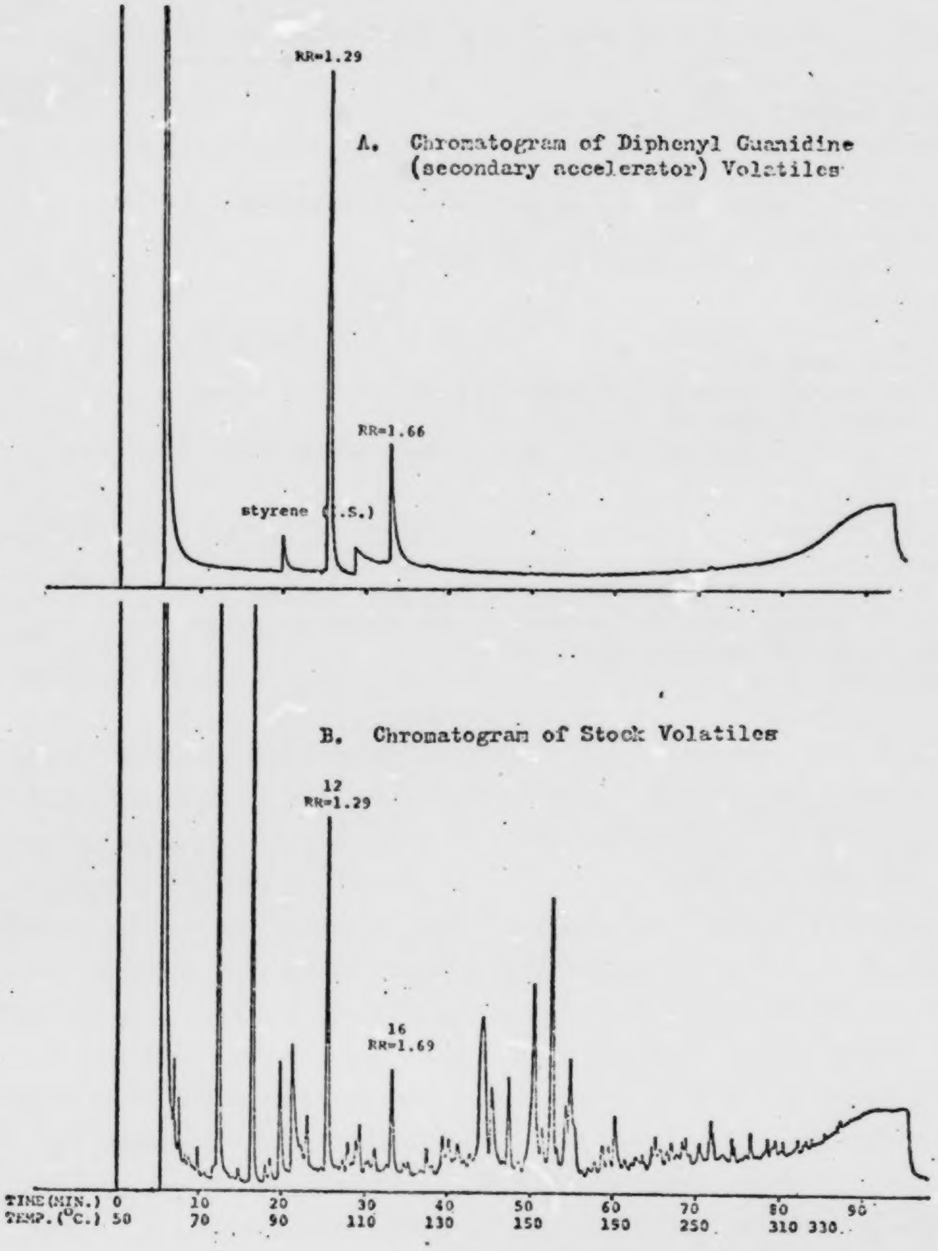


Figure 12. Retention time comparison of volatiles from a rubber additive with those from the compounded stock (relative to styrene).

Table 3. Parameters for gas chromatography-mass spectrometry

Gas Chromatograph
Model: Hewlett Packard 5700 A
Parameters: Same as given in table 2, except temperature program from 50 to 180°C at 2°/min
Separator: Single stage silicone membrane separator. Environmental Devices, Inc., Model 210
Temperatures: Inlet, separator at 200°C

Mass Spectrometer
Model: Hewlett Packard 5930-A Dodecapole Mass Spectrometer with 5932-A Data System
Resolution: 4 times mass number over entire mass range
Mass range: 33-350 amu
Scan rate: 100 amu/sec plus 6 sec delay between scans (10.5 sec/cycle)
Mass stability: ± 0.1 amu
Detector: Bendix Continuous Dynode Electron Multiplier
Temperature: Ion source at 200°C, Mass Filter at 110°C
Ion source: 70 eV Tungsten-Rhenium Filament (magnetically constrained), emission current at 250 μamp, target at 220 μamp (88 percent efficiency)

Table 4 lists the unusual assortment of compounds identified in the stock effluent. The oligomers of butadiene are quite abundant, especially the dimer, 4-vinyl-1-cyclohexene (which is primarily responsible for the stock's characteristic odor). Other known oligomers present include 1,5-cyclooctadiene (dimer) and the 1,5,9-cyclododecatriene trimers. Peaks 27, 28, and 29 are listed as butadiene trimers, although structures cannot be assigned. The general appearance of their spectra (especially the molecular ion at *m/e* 162) and the cis-polybutadiene rubber suspected source indicate this to be the case. The presence of toluene, which represents the largest resolved peak (peak #5), was also confirmed. Although its particular spectrum is common of other C_7H_8 hydrocarbons, e.g., cycloheptatriene, the gas chromatographic retention times match perfectly. Other confirmed compounds include styrene (residual monomer from the styrene-butadiene rubbers), N-*sec*.butylaniline (an impurity from the antiozonant), benzothiazole (from the accelerator), and several alkyl benzenes and naphthalenes (probably from the aromatic oil). One compound, *t*.butylisothiocyanate, was tentatively identified from its mass spectrum and the estimated boiling point of the peak.

Table 4. Compounds identified in the tread stock effluent

Peak No.	Compound	Method of Identification[a]	Probable source
5	toluene	MS + GC	Polybutadiene rubber
6	4-vinyl-1-cyclohexene	MS + GC	Polybutadiene rubber
7	ethyl benzene	MS + GC	Aromatic oil
8	m + p-xylene	MS + GC	Aromatic oil
9	styrene	MS + GC	Styrene butadiene rubber
10	_t_.butylisothiocyanate	MS + BPest	N-_t_.butyl-2-benzothiazole sulfenamide
11	1,5-cyclooctadiene	MS + GC	Polybutadiene rubber
22	benzothiazole	MS + GC	N-_t_.butyl-2-benzothiazole sulfenamide
23	N-_sec_.butylaniline	MS + GC	N-phenyl-N'-_sec_.butyl-p-phenylenediamine
24	1,5,9-cyclododecatriene	MS + GC	Polybutadiene rubber
25	methyl naphthalenes	MS + GC	Aromatic oil
26	1,5,9-cyclododecatriene	MS + GC	Polybutadiene rubber
27	butadiene trimer	MS + BPest	Polybutadiene rubber
28	butadiene trimer	MS + BPest	Polybutadiene rubber
29	butadiene trimer	MS + BPest	Polybutadiene rubber
30	ethyl naphthalene	MS + GC	Aromatic oil
31	dimethyl naphthalene	MS + BPest	Aromatic oil
32	dimethyl naphthalene	MS + BPest	Aromatic oil

[a] Identifications are based upon interpretation and/or comparison of mass spectra with standard spectra (MS), upon comparison of gas chromatographic retention times with those of analytical standards (GC), and upon an estimation of the boiling point, derived from the gas chromatogram and comparison with the known value (BPest).

Field Sampling and Analysis

Field sampling was performed using a charcoal tube method which has served numerous industrial hygiene applications (refs. 36,40,41,46,47). Glass tubes (70 mm x 4 mm I.D.) were packed with two sections of 25/40 mesh activated cocoanut charcoal (Fisher Scientific), weighing 100 ± .2 mg and 50 ± .2 mg, respectively. Silane-treated glass wool (2 mm length) was used to separate the charcoal sections and to plug the ends of the tubes, which were sealed with plastic caps. Uniformity tests showed the prepared tubes to have a mean pressure drop at constant one liter/min flow rate of 75.94 mm mercury and a standard deviation of 2.52 mm or 3.32 percent.

Samples were collected in a press room where a large volume of bias-ply passenger tires containing the selected tread stock were cured. On the sampling dates, roughly 2/3 of the "Bag-O-Matic" presses in this area were committed to these tires, the remaining ones being used for heavy service tires. Two sampling locations were selected, one directly in the center of the passenger tire curing area and the other at its periphery (away from heavy service tire curing).

Four battery-operated personnel sampling pumps were attached to convenient structures, e.g., ladders and pipes, at each of the two locations. Randomly selected charcoal tubes were positioned vertically above each pump (at eye level) with plastic tubing so that air entered the 100 mg charcoal section. Nine samples were collected for 15-, 30-, and 45-minute periods over 6 hours at flow rates between 1.0 and 1.5 liter/minute.

Quantitative analyses were performed in the following manner. The 100 mg charcoal section of each tube was placed in a 1 ml microreaction vessel; 500 μl of spectral grade CS_2 were added and the vessel was capped with a Teflon-lined rubber septum. CS_2 was selected as the eluting solvent since it does not produce a quantitative response on the flame ionization detector. After 4 hours duplicate 3 to 5 μl aliquots of each extract were injected into the gas chromatograph under the same conditions as previously established (table 2). A compound's presence was confirmed by comparing its retention time with that of a standard; quantitation involved extrapolation from a calibration curve based upon peak heights. Subsequent analysis of the 50 mg charcoal section defined the extent of breakthrough and the reliability of the data.

Figure 13(A) is a typical chromatogram for a 100 mg charcoal section (45 min. sample) eluted with CS_2. Note that attenuation covers two orders of magnitude with the early eluting peaks being more abundant. Figures 13(B) and (C) are chromatograms of eluates of the 50 mg sample backup section and 100 mg control sections, respectively. It is apparent that there was no breakthrough for the sampling intervals selected.

The chromatograms indicate that the atmosphere within the plant was more complex than that generated from the isolated tread stock. However, several previously identified peaks were confirmed within the mixture. These compounds are listed in table 5, once again in order of elution. Substances released from the polymeric constituents of the stock predominate in this group of compounds. The oligomers of butadiene, for instance, are easily distinguished.

Table 5. Relative retention times[a] and desorption efficiency factors[b] for selected compounds in a passenger tire press room

Compound	Relative $\text{Retention}_{\text{field}}$	Relative $\text{Retention}_{\text{standard}}$	Desorption Efficiency
toluene	0.60	0.62	99.7
4-vinyl-1-cyclohexene	0.82	0.83	103.0
ethyl benzene	0.89	0.92	101.3
styrene	1.00	1.00	85.5
1,5-cyclooctadiene	1.13	1.16	102.0
1,5,9-cyclododecatriene(1)	2.53	2.55	71.4
1,5,9-cyclododecatriene(2)	2.69	2.66	71.4

[a] Retention times relative to styrene.

[b] Average efficiency of triplicate extractions (1.0 µl of compound from 100 mg 25/40 mesh charcoal with 500 µl CS_2).

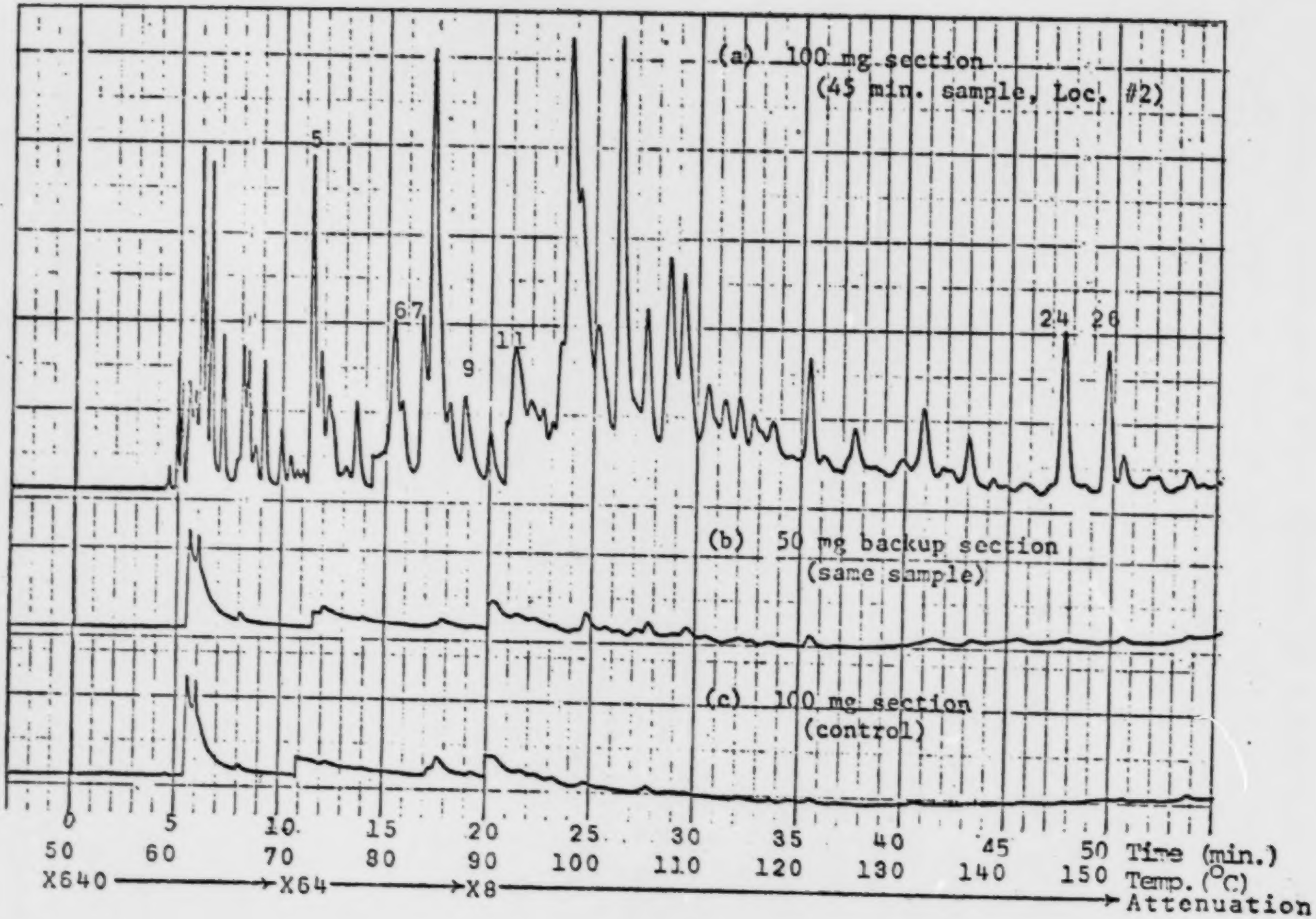


Figure 13. Chromatograms of charcoal tube eluates.

Table 5 also included CS_2 desorption efficiencies for those compounds which were confirmed. These values were determined experimentally by triplicate desorption trials of 1.0 µl of each substance from 100 mg of charcoal with 500 µl of solvent. The efficiencies are acceptable and range from 71.4 percent to 103.3 percent.

Table 6 lists airborne concentrations of the six compounds confirmed in the press room. These values are based upon duplicate analysis of each sample and incorporate desorption efficiency factors from table 5. On the sampling dates, concentrations ranged from a high of approximately 1100 ppb for toluene to roughly 7 ppb for 1,5-cyclooctadiene. These data represent greater than 99 percent confidence that the sample means were within one standard deviation of the true mean concentrations. Standard deviations for these samples are consistent, averaging 22.3 percent of the mean.

The substances selected for quantitative analysis were present throughout the range of resolution of the gas chromatographic system. By judging relative peak heights and attenuation factors for unknown peaks in figure 13-A and by assuming similar FID response and desorption efficiency factors, it is possible to bracket concentration ranges of these substances. Thus, the compounds in the highest attenuation group (X 640) would be between 0.3 and 1.5 ppm, those in the intermediate group (X 64) at 0.1 to 0.2 ppm, and those in the lowest group (X 8) between 0.005 and 0.030 ppm.

CONCLUSIONS

This study indicated that an unusual assortment of compounds is discharged during rubber vulcanization. Substances identified in the effluent from an isolated tread stock included styrene, butadiene oligomers, alkyl benzenes and naphthalenes, and some specific nitrogen and sulfur compounds. The presence of several of these substances, principally the butadiene oligomers, was confirmed in the tire plant where the stock was cured.

Regarding the source of these compounds, the results indicated that primary discharges were released from individual additives and were not products of chemical reactions within the rubber matrix. The largest single source of volatiles in the stock was the blend of polymers which also represented the bulk on a weight basis. Contributing in lesser amounts were ac-

Table 6. Air concentrations of selected compounds

Compound	Location[a]	1	2	3	4	5	6	7	8	9	Mean	Std. Dev.
toluene	1	1500	1290	1190	887	992	1530	1240	832	660	1120	301
	2	1000	747	1210	1460	1240	1340	1130	1180	1140	1160	202
4-vinyl-1-cyclohexene	1	84.5	97.7	66.1	56.0	70.6	77.7	71.6	60.6	54.4	71.0	8.42
	2	118	84.7	112	117	62.6	74.3	77.3	90.3	94.3	92.3	19.9
ethyl benzene	1	81.6	126	69.0	53.4	82.8	90.0	86.6	60.5	53.8	78.2	22.7
	2	121	99.0	121	178	79.7	88.9	101	118	98.0	112	28.8
styrene	1	96.3	130	79.4	61.5	83.2	86.7	95.6	67.5	61.6	84.6	21.5
	2	118	110	130	146	76.5	93.0	101	114	108	111	20.2
1,5-cycloocta-diene	1	8.19	7.74	5.95	4.88	7.08	6.39	7.37	4.61	4.22	6.27	1.44
	2	6.08	4.56	7.33	8.84	5.58	6.34	6.42	6.55	6.35	6.45	1.17
1,5,9-cyclododeca-triene	1	8.68	8.64	5.68	5.86	8.37	7.13	9.22	5.61	5.70	7.21	1.52
	2	16.4	17.2	26.5	14.8	10.6	14.8	10.3	16.2	15.4	15.8	4.70

[a] Location 1 directly in center of passenger tire curing area.
Location 2 at periphery of passenger tire curing area.

celerators, activators, antidegradants, and oils. It is significant that for the tread stock tested, all identified substances were either impurities or decomposition products.

Chromatograms of charcoal tube samples collected in the tire plant revealed a substantial number of peaks not present in the isolated tread stock effluent. Judging from their low boiling points, these substances may have been volatilized from nonstock ingredients such as solvents used in cements and bonding agents.

With regard to exposure levels, both laboratory and field data point to low boiling compounds as being orders of magnitude more prevalent than higher boiling components. Concentrations ranged between 1 and 2 ppm for substances in the C_6 to C_8 boiling region, then dropped to roughly 0.1 to 0.2 ppm for those in the C_8 to C_{10} range; higher boiling compounds (greater than C_{10}) were found at parts per billion levels. Instantaneous exposures may have been higher (e.g., immediately upon press opening) but were undoubtedly of short duration (seconds), given the high degree of turbulence and mixing.

For the stock and process investigated, the working environment did not appear to be overtly hazardous. Concentrations were so low that acute toxicity problems seem unlikely. On the bases of current toxicological data, chronic health effects are also questionable at these exposure levels. However, since little has been published concerning the carcinogenic potential of those compounds identified, significant health effects cannot be ruled out.

A comparable mixture of compounds would probably be discharged from similar vulcanization processes. The presence of residual monomers and other polymeric impurities, for instance, would be expected at the highest concentrations. Impurities from other compounding ingredients, especially the antidegradants, accelerators, and oils, may also be found at lower levels.

It appears likely that certain compound classes which have been associated with cancer may be discharged from curing processes. Aromatic amines present as impurities in the phenylenediamine antiozonants serve as an example, since such a compound was identified in the selected stock effluent (N-sec.butylaniline). Future techniques which are specifically designed for the sampling and analysis of aromatic amines would be useful in assessing this possibility.

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DISCUSSION

MR. PAUL KENT (Research Corporation of New England, Wethersfield, Conn.): Your tire presses were discharging their emissions into the general room ventilation in that building?

DR. RAPPAPORT: That is correct.

MR. KENT: Wouldn't it be much wiser if these were exhausting into individual units directly rather than into general ventilation?

DR. RAPPAPORT: I think the question is academic, but it is entirely possible that if the effluents were released into specific ventilation units, the concentrations remaining in the general room air would be lower.

MR. KENT: I do not think it is academic. It is an especially common situation in industrial ventilation because, if you capture the emissions and get them out of the general ventilation, you not only help solve your area pollution problem, but also an industrial hygiene problem.

DR. RAPPAPORT: Well, I agree. I have never been in a tire plant where the cure presses were differently ventilated, but I am sure it would be possible.

MR. KENT: I suppose it would be a large capital outlay on the present plants.

MR. RICHARD WALKER (Rubber World magazine, Akron, Ohio): Are there any plans to continue this type of study in those plants, where the press operator has to be next to the press and is subjected to a greater variety of material?

DR. RAPPAPORT: To my knowledge there are no plans at the present time for extending this work to other processes. You might ask Dr. Harris, who is with the University of North Carolina, if he does plan to continue this study. You might also ask Dr. Burgess of Harvard, which is conducting a similar study, if they plan to extend their work to various types of processes. To my knowledge there is no such work in progress at this date.

DR. SAM CHA (Research Corporation of New England, Wethersfield, Conn.): Have you made any indentifications of compounds with boiling points lower than C_6?

DR. RAPPAPORT: No, I have not. We know that certain compounds are going to be lost in the vulcanization process, including gases and very volatile liquids. In this particular investigation we did not pursue such identifications for purposes of convenience. Since we did not have a gas chromatograph - mass spectrometer system available on the project, we could not make the necessary manifold modifications for gas analysis. However, I think it is something that should be done in the future. I believe the Harvard people are working on that particular problem right now.

AIRBORNE PARTICULATE DEBRIS FROM RUBBER TIRES

William R. Pierson, Ph.D., and Wanda W. Brachaczek*

Abstract

Airborne particulate matter from rubber tires has been detected in the atmospheres of two vehicle tunnels and in the open air. The amount is of the order of 20 percent as great as the amount of particulate matter from vehicle exhausts, and represents some 5 to 10 percent of the tread material that disappears from tires in use.

Tread rubber was found on tunnel walls and in roadside dust, dustfall, and topsoil. A material balance shows that most of the material lost by tires in service is particulate matter, of which only a small fraction is airborne.

INTRODUCTION

The rate of wear of tire-tread rubber in the United States can be estimated at some 600,000 metric tons per year. By comparison, exhaust emissions of particulate matter from gasoline-powered vehicles in 1970 are estimated at 270,000 metric tons (ref. 1). In view of the tonnages just cited and of the attention that has been paid to exhaust particulates, it would seem appropriate to try to ascertain what happens to this tire-tread material. The present work was undertaken for that purpose. We especially wish to know whether rubber tires produce particulate matter that remains airborne for long periods and hence constitutes an air pollutant in the usual sense.

It has been commonly assumed (refs. 2,3) that significant amounts of such material are to be found. But until the recent work of Cardina (refs. 4,5), Brachaczek and Pierson (ref. 6), Pierson and Brachaczek (refs. 7,8), and Dannis (ref. 9), there had been only a few efforts to test this assumption. Investigations in earlier years have been as follows:

Thompson et al. (ref. 10) reported evidence of tire-wear debris in sweepings from tunnels, recapping operations, the National Bureau of Standards tire-testing machine, and a parking garage, by means of pyrolytic gas chromatography. They did not attempt a quantitative estimate, nor did they determine what fraction of the particles were small enough to have remained suspended for a significant time. They did not collect samples of airborne material.

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*Scientific Research Staff, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan 48121.

Brock (ref. 11) employed optical microscopy coupled with pyrolytic gas chromatography to examine aerosol samples collected along California roadways. He found the following types of particles:

1) Black particles about 40 microns × 100 microns, like wear particles from high-cornering wear. The pyrogram gave a strong SBR signal. (SBR = styrenebutadiene rubber, a major copolymeric hydrocarbon used in tire treads.) Nearly all of these particles appeared to be tread rubber particles.
2) Mixed rubber/nonrubber particles. The pyrogram gave a SBR signal of intermediate strength.
3) Small (down to 1 micron) black particles. The pyrogram showed no SBR.

Brock estimated that less than 5 percent of the particles overall were black and possibly rubber, some of these undoubtedly being nonrubber (oil, soot, etc.)

Laboratory experiments (refs. 12,13,14,4) indicate that only a small part of the material from tread wear is in gaseous form. The bulk of the material in those experiments evidently is emitted as particles, most of them large and nonsuspendable. Laboratory studies, however, are usually unable to simulate the behavior of a tire on a vehicle driving down the road, as is well known in the tire industry (ref. 15). It is clear from a review of the literature on tire wear mechanisms and rates that there are several wear modes and that these diverse modes will be very dissimilar with respect to the amounts of particulate matter produced per unit distance traveled, the size distributions of the particles produced, and the apportionment of the removed material between volatile products and particles. An investigation into the importance of airborne tire-particulate debris as an air pollutant should take cognizance of this. For example, an experiment carried out where Schallamach patterns develop, indicating severe conditions seldom experienced in the United States, can hardly be expected to provide insight regarding the air in the United States.

METHOD

Roadway studies were chosen in preference to laboratory studies for the reason just cited. The problem then is to distinguish between the aerosol produced by vehicles and the aerosol produced by extraneous sources. This distinction was accomplished at vehicle tunnels, which are continuously ventilated with large amounts of outside air, by sampling simultaneously the air at the intake and the air in the tunnel. The difference in concentration of any component between the two points is attributed to the traffic in the tunnel. (This procedure has been employed before (refs. 16-20) to estimate atmospheric contaminants produced directly or indirectly by motor vehicles).

The collected aerosol samples were chemically analyzed for substances that signify tire-tread debris. They were analyzed also for substances that signify exhaust particulate from gasoline engines, to provide a benchmark for comparison between amounts of tire particulate and gasoline-engine exhaust particulate-tire particulates from all types of vehicles vs. exhaust particulates from automobiles and other gasoline-powered vehicles.

The substances assayed as a measure of tire-wear debris were zinc, total carbon, and SBR (the commonest rubber hydrocarbon in tire treads). Zinc is present in all truck and automobile tire treads (ref. 21) in amounts approximating 1 percent. Carbon (free plus combined) constitutes about 91 percent of a tire tread, by weight.

The substance assayed as a measure of exhaust particulate was lead. Bromine was sometimes measured also. Both elements arise almost solely from gasoline-engine exhaust, although the bromine in airborne exhaust particulates does become depleted with time, as shown by our work and that of others (refs. 22-24). Diesel trucks of course produce tire wear but no lead or bromine.

Air sampling was also done at open-air sites, in order to cover a wider range of conditions than is available in tunnels. Zinc measurements here are of little value, because of the high ambient Zn levels. SBR is still a good indicator, however, since most of the SBR used in the United States is used in tires (refs. 25,26,27). Lead is a reliable indicator of exhaust particulates.

ANALYTICAL PROCEDURES

Zn, Br, Pb. Samples were analyzed for Pb by atomic absorption and anodic stripping voltammetry; for Br by neutron activiation analysis; and for Zn by atomic absorption, anodic stripping voltammetry, and neutron activation analysis. The neutron activation analyses were carried out nondestructively by irradiation in the reactor at the University of Michigan followed by X-ray spectrometry with a Ge(Li) detector and 4096-channel analyzer. In the later experiments, after the reliability of the Pb procedures had been satisfactorily established, Br analysis was dispensed with. Similarly, activation analysis for Zn was eventually discarded after the other two Zn procedures became established.

SBR. Infrared spectroscopy was employed to analyze for SBR. The styrene-butadiene copolymer, usually made for tire treads in a formulation consisting of 23.5 percent styrene by weight and the remainder of 1,3 butadiene (ref. 21), has a distinctive infrared spectrum (figure 1). The SBR was isolated and analyzed as described elsewhere (ref. 6). Briefly, Soxhlet extraction into benzene removes most organic material plus any benzene-soluble (devulcanized) SBR that is present. Subsequent Soxhlet extraction(s) with orthodichlorobenzene ($\equiv oCl_2\phi$) in a stream of oxygen extracts the vulcanized SBR. Infrared spectra of KBr pellets made from the benzene and $oCl_2\phi$ extracts yield the amount of SBR by measurement of the intensities of the absorption lines at 10.35 and 14.3μ. Duplicate samples to which a known amount of standard SBR tread vulcanizate (ASTM Standard E249-66) has been added prior to extraction provide a check of good recovery. The amount added is chosen in each case to be comparable to the amount found without addition. Analysis by gel permeation chromatography shows that the extraction in orthodichlorobenzene and oxygen results in significant spreading of the molecular-weight distribution in the direction of lower molecular weight, but no significant loss of copolymer.

Pyrolytic gas chromatography was investigated as an alternative means of identifying SBR in the filter samples. The pyrolysis of SBR gives styrene among the products, and Thompson et al. (ref. 10) considered the detection of styrene to signify the presence of SBR in their samples. Unfortunately, our samples often contain substantial quantities of Diesel exhaust particulate which, we find, gives much styrene on pyrolysis. Moreover, other features of the pyrogram of Diesel exhaust particulate resemble that of SBR. Undoubtedly there are other substances in atmospheric aerosols that will cause similar difficulties. Thus, the pyrolytic gas chromatography technique seems inapplicable to our study.

Total Carbon. Analysis was carried out by Cu-catalyzed combustion with O_2 in an induction furnace and assay of the CO_2 evolved. The CO_2 was measured by an automatic CO_2 analyzer with a thermal-conductivity cell.

Specific Surface Area. These analyses were instituted to assess the capacity of aerosol particles to adsorb SBR molecules before or during the extractions. By the time it had become apparent that this potential source of error in the infrared determination of SBR was probably not serious, it had also become apparent that a knowledge of specific surfaces of the aerosols in this study was important in its own right, and therefore the measurements were continued. These measurements were made by the conventional Brunauer-Emmett-Teller method, from krypton adsorption at 77°k in a known weight of sample preconditioned by pumping to an absolute pressure of 10^{-5} torr at room temperature.

GRAVIMETRIC FACTORS FOR ZINC AND SBR

Zinc. Neutron activation analysis of automobile tire treads from a number of manufacturers yielded an average Zn content of 1.0 percent, somewhat lower than the generally accepted average (1.7 percent, ref. 21). The value similarly found for the ASTM E249-66 standard tread vulcanizate is 1.01 percent, in agreement with the recipe value (1.08 percent); accordingly, we believe that our measurement is reliable. Truck tire treads have approximately the same Zn content as automobile tire treads (ref. 21). We therefore take 1.0 percent as the average Zn content of tire tread.

Detergent lubricating oils contain about 0.12 percent Zn. Emission of Zn from this source is said to result in a Zn/Pb mass ratio of 0.006 in the exhaust particulate matter from gasoline engines operating on leaded fuel (ref. 28). Ratios ranging between 0.0013 and 0.011 have been reported in chassis-dynamometer tests (ref. 29).

From neutron-activation results showing 0.2 and 0.03 ppm Zn in regular and premium gasoline, respectively, we conclude that the detergent oil must be the source of some 90 percent of the exhaust particulate Zn. But detergent oils for Diesel engines also contain Zn (about 0.1 percent). Neutron activation analysis of two Diesel exhaust particulate samples gave 44 and 96 ppm Zn, comparable with the 30 ppm or thereabouts reported by Frey and Corn (ref. 30).

We shall consider an amount of Zn corresponding to a Zn/Pb ratio of 0.006 to be attributable to gasoline-engine exhaust particulate in our samples. We shall ignore the Zn from Diesel exhaust, lacking a cognate by which to estimate it.

SBR. Production and consumption figures (refs. 31-27) show that SBR comprises slightly more than 50 percent of the rubber hydrocarbon used in tire treads. In turn, the aggregate rubber hydrocarbon in a tire tread is about 50 percent of the finished material (ref. 21). Hence, the average SBR content of tire tread is about 25 percent. This is the figure we adopt.

To check this adopted figure, we analyzed the treads of 47 tires, all of different descriptions, and found the following averages: five passenger tires, 24.6 percent SBR; 34 truck tires, 7.0 percent SBR; nine truck recaps, 22.7 percent SBR. The numbers of truck recap and nonrecap tires on the road are comparable, and thus the average truck tire tread is effectively 15 percent SBR.

Production and consumption figures (refs. 26,27,33) indicate that polybutadiene constitutes about 16 percent of the rubber hydrocarbon in tire treads. Transolefinic linkages in polybutadiene will have the same 10.35-μ infrared absorption as SBR, thus enhancing the apparent amount of SBR in the sample insofar as the 10.35-μ line is used in the estimation. Much of the polybutadiene in treads is cis rather than trans, and thus the enhancement is slight. We ignore this perturbation, especially since it comes from tires anyway.

ALLEGHENY TUNNEL EXPERIMENTS

The Allegheny Mountain Tunnel of the Pennsylvania Turnpike is located about 19 km east of Somerset, Pennsylvania, in a rural setting. It runs approximately east-west through Allegheny Mountain some 125 meters beneath the summit. It is a four-lane, two-tube tunnel (two eastbound lanes through one tube, two westbound lanes through the other), 1.85 km long, with a slight (ca. 0.5 percent) grade downward toward the east. The easternmost 45 meters of the eastbound tube is on a curve (radius of curvature 332.8 meters) to the left. The surface is asphalt and is always dry over most of its length, even in the wettest weather. The speed limit was 50 mi/hr (80 km/hr) during the 1970 experiments and 55 mi/hr during the subsequent experiments. There is some braking but no legal lane-switching, i.e., only a minimal amount of maneuvering in the tunnel.

These conditions correspond to a mild-wear situation, with expected rates between 0.002 and 0.004 mils per mile (refs. 35,36), or 0.01 to 0.03 grams per mile for automobile tires. Truck tire wear rates, in grams per mile, will be slightly less than rates for standard-bias automobile tires. (In contrast, the average wear rate for automobile tires in the United States is about 0.15 grams per mile per tire, by our estimate.)

Automobile traffic in the tunnel fluctuates markedly with time, being highest in summer, during daylight (figure 2), and on weekends (figure 3). Truck traffic is relatively constant except for a weekend subsidence. Truck traffic in the tunnel keeps to the right-hand lanes.

The ventilation system employs intake fans above each end of the tunnel. Ducts carry the intake air from each end toward the center, where it enters the tunnel through overhead louvers. The air provided by this ventilation system is augmented by air coming in through the vehicle entrance portal of each tube under the influence of the ramming action of the traffic, reinforced in the case of the eastbound tube by a natural flow from the west. There is no exhaust system as such. All of the air outflow from the tunnel issues from the vehicle exit portals, at velocities measured in the eastbound tube between 6 and 9 meters per second.

Traffic volume was monitored during these experiments by a traffic counter installed at the west end of the eastbound tube. Apportionment between automobiles, gasoline-powered trucks, and Diesel-powered trucks was ascertained by frequent counting by eye (figure 2). Our own traffic observations were supplemented with traffic records from the Turnpike Commission.

Air Sampling Experiment 8/1/73 (Eastbound tunnel only)

Sample Collection. Air was sampled continuously for the period August 1 through August 13, 1973, at each of four stations:

1) East (exit) portal of eastbound tunnel;
2) West (entrance) portal of eastbound tunnel;
3) West intake fan room for eastbound tunnel;
4) East intake fan room for eastbound tunnel.

The portal stations were set up 5 to 7 meters inside the portals, 80 to 95 cm to the left of the left-hand lane, and 1.4 to 1.8 meters above the roadway.

At each station, three samples were collected simultaneously:

1) 142 mm diameter mixed-cellulose-ester membrane filter, mean pore flow diameter 0.2μ, sampling rate about 100 liters/minute, for determining specific surface, total carbon, and SBR;
2) 47 mm diameter cellulose-acetate membrane filter, pore size 0.2μ, sampling rate about 12 liters/minute, for determining Pb and Zn;
3) Standard Hi-vol sampler with 8" x 10" glass fiber filter, sampling rate about 1 meter^3/minute, for determining total carbon and SBR.

The membrane filters were oriented with their collection surfaces downward, and enclosed in settling chambers with multiple baffles to prevent access by particles larger than an estimated 20 to 100 microns. The units in the intake fan rooms were mounted in standard weather-station shelters. Air velocity through the membrane filters ranged up to 30 cm/second. Filtration efficiency under these circumstances should be effectively 100 percent irrespective of aerosol particle size (ref. 37). Air was drawn through the membrane filter by means of metal-bellows diaphragm pumps (which have no leak to the outside) and exhausted through calibrated (±1 percent) temperature-compensated dry-test meters for determination of sample volume.

Owing to the design of the standard Hi-vol sampling units, some collection of particulate matter in the nonsuspendable size range (>10μ) occurs. Recent studies (refs. 38,39) have shown that large (20-200μ) particles generally make up much of the particulate mass collected near ground level by such instruments.

The SBR size distribution at the East Portal was determined by means of a standard Hi-vol cascade impactor with glass-fiber backup filter and impingement surfaces, operated at a flow of approximately 570 liters per minute as prescribed (refs. 40,41). Losses of particles within an instrument of this design are said to be important under certain conditions (ref. 39).

Dustfall samples were collected at the end of the experiment from surfaces which had been clean at the outset.

Results. The airborne particulate collected at the East Portal is a fine black fluffy cohesive powder. Some of its other properties are listed in table 1. The diurnal and weekly variation of the airborne gross particulate concentration (figure 4) follows the pattern of truck traffic rather than automobile traffic (figures 2 and 3).

SBR was found in all East Portal samples, as exemplified by the spectra shown in figure 5. The results from all the East Portal Hi-vol analyses are plotted in figure 6. The average airborne SBR from these analyses is 0.61 μg/m^3. The SBR collected on the membrane filter is far lower, 0.20 μg/m^3, than on the Hi-vols, suggesting that most of the SBR collected in the Hi-vols consists of settleable material; the membrane filter would collect almost none of the settleable material because of the (already described) way it was set up. This speculation is supported by the size distribution (table 2), and by the SBR content of the dustfall (table 3), as well as by the SBR content of the debris in the gutters (discussed later).

The specific surface after oCl$_2\phi$ extraction is comparable with that of carbon black (60 to 120 meter^2/gram). Carbon black is capable of adsorbing some 200 mg SBR per gram of sample even in boiling oCl$_2\phi$ (refs. 42-44).

Standard addition experiments on portions of each sample, using standard tread vulcanizate (ASTM E249-66), indicated that the average SBR yield was 65 percent for the East Portal Hi-vol samples and 70 percent for the East Portal membrane samples. We consider these yields good, in view of the specific surfaces shown in table 1. The yields of SBR on the cascade-

Table 1. Properties of airborne particulate matter collected at East Portal of Allegheny Tunnel (Eastbound tube), 1-13 August 1973

Pb	4.4%
Zn	0.08%
Total C (free and combined)	56%
Residue after C_6H_6 extraction	86%
after O_2 + oCl$_2$0 extraction	76%
Specific surface, initial	31 meter^2/gram
after C_6H_6 extraction	57 meter^2/gram
after O_2 + oCl$_2$0 extraction	91 meter^2/gram
SBR (total all extracts)	0.1 to 0.5%

Table 2. Size distribution of airborne SBR collected at East Portal of Allegheny Tunnel (Eastbound tube) during August 1973 experiment

Aerodynamic diameter, microns[a]	Concentration of SBR in stated size range[b]
>7	0.07 μg/m^3
3.3-7	0.02 μg/m^3
2-3.3	0
1.1-2	0
<1.1	0.13 μg/m^3

[a] Calibration is from Wood and Erickson (ref. 40) and Burton et al. (ref. 41).

[b] Owing to the low SBR recovery observed in standard-addition experiments on portions of the impactor stages, these numbers are subject to considerable uncertainty and should not be relied upon except to indicate the dominance of very small and very large particles.

Table 3. Properties of dustfall collected inside East Portal of Allegheny Tunnel (Eastbound tube), 1-13 August 1973

Pb	0.53%
Zn	0.187%
Total C (free and combined)	20%
Redidue after C_6H_6 extraction	87%
after O_2 + $oCl_2 0$ extraction	?(>52%)*
Specific surface, initial	0.3 meter^2/gram
after C_6H_6 extraction	1.3 meter^2/gram
after O_2 + $oCl_2 0$ extraction	7.7 meter^2/gram
SBR (total all extracts)	2.3%

*Some material was lost in transferring.

impactor stages, on the other hand, were low (down to 15 percent). No correction for yield is applied in reporting our results.

SBR could not be detected in any of the samples collected at the intakes. These are the only air samples in the entire program in which SBR was not detected.

Average airborne concentrations of the various constituents are listed in table 4. It can be seen that the injection of gross mass, Pb, C, and SBR into the tunnel air by vehicles is considerable, relative to the respective background values. The readings at the West Portal are intermediate in character between background and East Portal values, as would be expected.

Table 4 shows that much of the SBR is extracted by benzene. We observe that this is the rule for SBR in environmental samples. In contrast, only 2 to 3 percent of the SBR in a sample of fresh tread vulcanizate would have been extractable into benzene. This indicates that considerable chemical breakdown of the vulcanizate network occurs before the particles are collected in the present experiment. The residence time of air in the tunnel is of the order of 2 minutes, and therefore the breakdown

Table 4. Aerosol concentrations at Allegheny Tunnel, experiment 8/1/73, Eastbound tube

	Average concentration, $\mu g/m^3$					
					SBR	
	Gross	Pb	Zn	C	C_6H_6 extract	$\Sigma(O_2 + oCl_2\phi)$ extracts
East (exit) Portal						
Membrane filter	205	9.3	0.167	111	0.141	0.060
Hi-vol filters	210				0.255	0.356
West (entrance) Portal						
Membrane filter	71	1.42	0.068	19.0		
Hi-vol filters	78				0.04	0.05
East intake fan room	64	0.30	0.053		0(<0.019)	0(<0.04)
West intake fan room	58	0.48	0.050	12.9	0(<0.015)	0(<0.029)

would seem to be rapid, perhaps occurring during the abrasion process itself. There is essentially no sunlight in the tunnel, and presumably no ozone (owing to the presence of nitric oxide); accordingly, rapid decomposition while airborne would seem unlikely. Samples analyzed for SBR months after collection show no greater benzene-extractable fraction than duplicates analyzed immediately, and hence we doubt that the process occurs within the deposit after collection.

Fan records and measurements of portal air velocities indicate that the total air flow through the tunnel during the experiment was $3.4 \times 10^8 m^3$, about 59 percent of it being through the fans. We multiply this figure by the increase of each species over background (i.e., the East Portal concentrations minus the intake fan-room average concentrations) to obtain, for each species, the amount generated in the tunnel during the experiment. These amounts are listed in table 5. From the $\Delta Zn/\Delta Pb$ ratio we see that nearly half of the ΔZn should be attributed to the lubricating oil in gasoline engines, leaving a "residual" $\Delta Zn/\Delta Pb$ of 0.007. On the other hand, Diesel exhaust cannot account for much of the observed Zn, since $\Delta Zn/\Delta Gross$ is at least 10 times the Zn content of Diesel exhaust particulate.

Table 5. Amounts of airborne particulate species generated inside the Allegheny Tunnel (Eastbound) during the period 1-13 August 1973

Species[a]	Grams
ΔGross particulate	5×10^4
ΔPb	3×10^3
ΔZn	40
ΔC	3×10^4
ΔSBR (membrane filters)	69
(Hi-vol filters)	210

$$\Delta Zn/\Delta Pb = 0.0129$$

$$\Delta SBR/\Delta Pb = \begin{cases} 0.022^{b} \\ 0.068^{c} \end{cases}$$

[a] The notation Δ means that the respective background levels (intake-fan-room levels) have been subtracted.

[b] Using East Portal membrane filter values.

[c] Using East Portal Hi-vol filter values.

It is immediately apparent in table 5 that airborne tire particulate is minor compared to airborne exhaust particulate or airborne total particulate from vehicles.

Traffic data indicate that light-duty vehicles (cars, motorcycles) logged 152,500 vehicle-miles, and heavier vehicles (trucks, busses) logged 40,900 vehicle-miles, in the eastbound tube during the period of the experiment. Using our observation that the latter category included almost no gasoline driven vehicles but was dominated instead by 5-axle (18-tire) Diesel trucks, we can estimate the following airborne particulate production rates based on our measurements:

Gross mass = 0.27 g/mile per vehicle, all categories;

Pb = 3.0×10^{-5} g/mile per tire, all categories (without motor-oil correction);

C = 0.17 g/mile per vehicle, all categories;

SBR = (5 to 16) $\times 10^{-5}$ g/mile per tire, all categories.

With 1 percent as the Zn content and 25 percent as the SBR content of the average tire in the tunnel, it appears that the airborne tire-particulate debris is of the order of only 10^{-3} gram/mile per tire. Clearly, the bulk of the tire debris in the tunnel is not airborne.

Gutter Experiment 9/12/73

The purpose of this experiment was to account for the rest of the tire-wear material, the presumption being that it consists of larger particles and hence should be found at roadside. This experiment was carried out in the eastbound tube to facilitate comparison to the results of the 8/1/73 experiment. We were fortunate that the tunnel maintenance schedule presented the opportunity for this experiment at a time not too far removed from the 8/1/73 experiment, although, in the interim, some shift in the makeup of the traffic had already occurred (just after Labor Day).

The tunnel has gutters along each margin of the roadway running the full length of the tunnel, divided by catch basins at intervals into sections (average length about 50 meters) that effectively cannot transfer material between them. There are also gutters at curb height running the full length of the tunnel on each side, which served to drain the walkways and walls. The latter set of gutters empties into, and contains far less material than, the roadway gutters. It seems reasonable to assume that nearly all settleable material will find its way into the roadway gutters, except for smaller amounts swept or carried out through the exit portal or attached to the wall tiles.

Procedure. In principle, the roadway gutters can be completely cleaned out, then the debris permitted to accumulate in them for a period of time during which a known number of vehicles traverse the tunnel, and then the accumulated debris can be collected and analyzed for SBR. To make the undertaking tractable, we concentrated on three sections marked off by catch basins, one near the West Portal, one at midtunnel, and one near the East Portal, of average length 50.2 meters each (i.e., 150.5 meters total, or 8.1 percent of the tunnel length). In each section we cleaned the gutters thoroughly on both sides of the roadway. One week later (9/19/73) we collected the material from these sections into canvas bags using a gasoline-powered industrial vacuum cleaner. The samples from the three parts of the tunnel were kept separate for analysis.

Each sample was sifted into three size fractions (<1mm, 1-2.38mm, >2.38mm). The fraction <1mm was divided by a solid sample divider to give samples small enough for analysis. The fraction 1-2.38mm was first cleared of straw, magnetic particles, and particles that were clearly rubber; each of these categories was analyzed, as was a known portion of the residue. The fraction >2.38mm was dealt with by culling out the rubber particles and chopping them up for analysis, discarding the rest. Analyses for Pb, Zn, and SBR followed the usual procedures.

Results. The analyses, in grams per meter of tunnel length, are listed in table 6. Averaged over the length of the tunnel, about 84 percent of the gross mass, 96 percent of the Pb and Zn, and 89 percent of the SBR are in the sub-1000-μ size range.

Traffic records indicate that 39,838 light-duty vehicles and 18,238 heavier vehicles traversed the eastbound tube during the 12-19 September accumulation period. Equating the former quantity with the number of cars and noting that the latter category is dominated by five-axle (18-tire) Diesel trucks, we find the following production rates for settleable particulate matter, averaged over the length of the tunnel:

Gross mass = 13.7 g/mile per vehicle, all categories;
Pb = 0.037 g/mile per gasoline-powered vehicle;
Zn = 5.6×10^{-4} g/mile per tire, all categories;
SBR = 1.41×10^{-3} g/mile per tire, all categories.

Table 6. Roadway gutter debris accumulated in Eastbound tube of Allegheny Tunnel 12-19 September 1973

	West (57.9 m)	Middle (42.0 m)	East (50.6 m)	Mean (weighted)
Total grams/meter	811	401	212	495
Pb grams/meter	1.08	1.14	0.54	0.91
Zn grams/meter	0.24	0.16	0.10	0.17
SBR grams/meter	0.44	0.49	0.36	0.43

Comparison with the results of the 8/1/73 experiment shows that at least 10 times as much SBR settles out as remains airborne.

Earlier Experiments

Air sampling was carried out on three previous visits. During some of these visits, air was sampled in the westbound tube. Background samples were taken in the fan rooms, on the hillsides uphill from the fan rooms, or in a radio tower atop the mountain. The shielding against collection of large particles was not as good in these earlier experiments.

Results are given in table 7. They are generally consistent with those shown in table 4. The westbound readings are higher than the eastbound readings, as would be expected from the prevailing wind and the roadway grade. During the 8/6/71 experiment the samplers were shut off at night to suppress the role of trucks; hence the unusually high Pb reading.

The average ΔZn/ΔPb ratio for 5/30-5/31/70 and 8/6-8/16/71 (i.e., the earlier experiments exclusive of "tunnel" samples collected actually outside the tunnel, or measurements where the background is in doubt) was 0.013, in agreement with the 8/1/73 results. SBR was assayed by infrared analysis in one experiment (footnote b, table 7).

From the fan records, air-speed measurements, and traffic records of the 8/6/71 experiment, airborne particulate generation rates were calculated:

Gross mass = 0.31 g/mile per vehicle, all categories;
Pb = 0.029 g/mile per gasoline-powered vehicle;
Zn = 5.9×10^{-6} g/mile per tire, all categories
(without motor-oil correction);

in reasonable agreement with the results from the 8/1/73 experiment.

Analyses of other samples collected during the 8/6/71 experiment are shown in table 8. The samples were obtained near the East Portal of the eastbound tube. The walkway-gutter sample consisted of all debris 14.4 to 19.4 meters inside the East Portal on each side of the tube. The wall samples were obtained by scrubbing 6 meter^2 of wall tile beginning 14.4 meters inside the portal. The roadside panels were framed glass-fiber mats set 35 meters outside the portal at road level about 20 meters away from the road.

Table 7. Earlier aerosol measurements at Allegheny Tunnel

	Aerosol concentration, μg/m^3				$\frac{Zn_{out} - Zn_{in}}{Pb_{out} - Pb_{in}}$
	Gross	Pb	Br	Zn	
5/28/70 - 5/30/70					
East portal eastbound	257	--	4.10	0.31	--
West portal westbound	375	--	7.39	0.40	--
East hillside	70	--	0.10	0.15	
West hillside	45	--	0.046	0.13	
5/30/70 - 5/31/70					
East portal eastbound	219	10.4	4.22	0.18	0.015
West portal westbound	221	10.9	5.27	0.16	0.013
East hillside	68	0.27	0.046	0.023	
West hillside	66	0.14	0.020	0.023	
5/31/70 - 6/2/70					
East median (10 m out of tunnel)	44	1.02	0.22	0.046	0.024
West median (10 m out of tunnel)	61	1.14	0.39	0.052	0.028
East hillside	33	0.19	0.024	0.027	
West hillside	34	0.10	0.015	0.022	
9/14/70 - 9/16/70					
East portal eastbound	193	3.78	1.18	0.19	<0
West portal westbound	246	7.90	3.59	0.21	0.001
Radio tower[a]	60	0.20	0.018	0.20	
9/17/70 - 9/20/70					
East portal eastbound	128	4.86	1.87	0.18	0.006
West portal westbound	175	8.79	3.60	0.18	0.002
Radio tower[a]	40	0.19	0.017	0.16	
8/6/71 - 8/16/71					
East portal eastbound[b]	264	17.2	--	0.286	0.012
East fan room	61	0.61	--	0.079	
West fan room	71	0.83	--	0.087	

[a] Readings at the radio tower may not be a valid measure of background--too far from the tunnel.

[b] SBR readings were also obtained (but by an infrared method shown by subsequent work (Brachaczek and Pierson, 1974) to lead to losses); C_6H_6 extract = 0.18 μg/m^3, $(O_2 + oCl_2\phi)$ extract (presence not sure) ≈ 0.02 μg/m^3.

Table 8. Roadside debris near East Portal of eastbound tube at Allegheny Tunnel in experiment 8/6/71

	Total Mass	Pb	Zn	C	SBR
Roadway gutter	--	0.19%	0.04%	8.8%	0.185%
Gutter, along walkway, g/meter	10.6[a,b]	0.030[a,b]	0.012[a,b]	1.8[a,b]	0.154[a,b]
Wall scrubbings, μg/meter^2	--	3025[b,c]	685[b,c]	--	9478[b,c]
Roadside dustfall panels	--	0.45%	0.11%	--	1.1%

[a] Grams per meter length of tunnel, in the walkway gutters along both sides of the tube.

[b] The accumulation period for this material was 14 days.

[c] Micrograms per square meter of tunnel wall.

The size distribution of the roadway-gutter material is shown in figure 7. To obtain this distribution, the sample was fractionated by means of sieves and each fraction was analyzed for gross mass, Pb, Zn, and SBR. The part of the distribution above 1000μ was obtained from the 9/12/73 gutter experiment. The SBR mass median diameter is seen to be approximately 140 microns.

From the geometry of the tunnel and the wall area scrubbed, and assuming emission of SBR to be isotropic about the roadway centerline, we estimate that the amount of SBR found on the walls corresponds to about 0.3 grams of SBR deposited on walls and ceiling per meter of tunnel length. In the 14 days since the previous tunnel washing, 166,894 light-duty vehicles and 38,117 heavier vehicles had traversed the eastbound tube. The tunnel washing leaves the walls and walkway gutters reasonably clean. Thus we can estimate the production rates per vehicle-mile, for material adhering to the tunnel walls:

$\text{Pb} = 1 \times 10^{-3}$ g/mile per gasoline-powered vehicle;
$\text{Zn} = 3 \times 10^{-5}$ g/mile per tire, all categories;
$\text{SBR} = 4 \times 10^{-4}$ g/mile per tire, all categories.

Similarly, for the walkway gutters:

$Pb = 3 \times 10^{-4}$ g/mile per gasoline-powered vehicle;
$Zn = 1.5 \times 10^{-5}$ g/mile per tire, all categories;
$C = 0.014$ g/mile per vehicle, all categories;
$SBR = 2 \times 10^{-4}$ g/mile per tire, all categories.

General

Table 9 summarizes the grams-per-mile estimates of particulate matter generated by vehicles in the Allegheny Tunnel. Not included are the unknown amounts of material swept out of the tunnel, dustfall on sidewalks, etc. It is immediately clear that 2 to 7 percent of the observed SBR particulate debris is airborne. (This in turn implies that no more than 2 to 7 percent of the SBR tread worn off takes the form of airborne particulate matter.)

The expected tire wear rate (0.01 to 0.03 grams per mile per tire) and the SBR content of tire tread implies that SBR should be released in the tunnel at the rate of 0.002 to 0.007 grams per mile per tire. The observed rate (last row of table 9) is a substantial fraction of the expected figure. A more detailed calculation, with 15 percent SBR for the average truck tire tread and 25 percent SBR for the average automobile tire tread (see earlier), indicates that the SBR we have found accounts for 50 percent to 100 percent of the estimated SBR worn off.

The expected wear rates also imply release of 10^{-4} to 3×10^{-4} grams of Zn per mile per tire. Comparison with table 9, bearing in mind that almost half of the airborne Zn shown there is probably due to gasoline-engine exhaust, shows that

a) no more than 5 percent to 30 percent of the tire wear in the tunnel becomes airborne particulate matter (even assuming tires to be the only source of airborne Zn in the tunnel aside from engine lubricant);

b) some of the settleable Zn probably comes from sources other than tires.

The second point is supported further by figure 7, which shows that the size distribution of Zn in the roadway gutter resembles that of the gross material rather than that of the SBR.

Table 9. Rates of generation of airborne and settleable particulate by vehicles eastbound in the Allegheny Tunnel (from experimental results)

	Airborne	Tunnel walls	Walkway gutters	Roadway gutters[a]	Total
Total g/mi/vehicle	0.29	--	0.083	13.7	14.1
Pb g/mi/gasoline-powered vehicle	0.025[b]	0.001	0.0003	0.037	0.06
Zn g/mi/tire, all kinds	$(3\text{-}6) \times 10^{-5}$[c]	3×10^{-5}	1.5×10^{-5}	5.6×10^{-4}	6.2×10^{-4}
C g/mi/vehicle	0.17	--	0.014	1.21	1.4
SBR g/mi/tire, all kinds	$(5\text{-}16) \times 10^{-5}$	4×10^{-4}	2×10^{-4}	1.4×10^{-3}	0.0022

[a] Average of the West, mid-tunnel, and East analyses, weighted according to the length of each section.

[b] Declined steadily from 0.029 to 0.019, 1971-1973.

[c] Not corrected for the presumed Zn contribution from engine lubricant. This contribution is expected to be nearly one-half of the airborne Zn.

It is obvious from table 9 and other data that SBR has a greater tendency to settle than does exhaust particulate. There is a subtlety, however: The SBR content of the walkway-gutter debris (1.5 percent) and dustfall (2.3 percent) far exceeds that of the roadway gutters (0.27 percent); and the SBR/Pb ratios in the wall scrubbings (~3), walkway gutters (~5), and dustfall (4.3) far exceed the ratio in the roadway gutter (~0.5 to 1) (tables 3,6,8). The size distributions (figure 7) show the same trend: Evidently the SBR, though predominantly nonsuspendable, is relatively deficient in the larger particles of the settled distribution when compared with Pb or gross mass.

DETROIT AND CANADA TUNNEL EXPERIMENTS

The "Windsor Tunnel," as it is often called, runs under the Detroit River and connects downtown Detroit with Windsor, Ontario. It is a two-lane, single-tube tunnel 1.57 km long, with substantial (up to ca. 5 percent) grades. The pavement is asphalt. The speed limit is 30 mi/hr. Normally there is much truck traffic. The air in the tunnel is circulated in four independent tunnel sections, each section having its own air-supply and exhaust systems. The two sections on the ends are called the "land" sections, and the two in the central part are called the "river" sections. We sampled the air systems for the river and land sections on the American side; there is a curve in the former section, and in the latter section the road goes into a sharp spiral. Samplers were placed next to the intake fans and in the exhaust chimneys at the vent building in Detroit, and in the intake and outlet ducts. Air velocities in the ducts (cross sections about 9 meter^2) are 5 to 15 meters/second, and in the exhaust chimneys (cross sections 11 to 14 meter^2) 2 to 5 meters/second.

The wear conditions in the tunnel are expected to resemble those for urban driving, where wear rates (ref. 45) are in the range of 0.02 to 0.04 mils per mile (0.1 to 0.3 grams per mile per tire). The intake fan room, situated as it is in the heart of Detroit, also serves as an open-air site 16 meters above ground level for assessing tire debris generated in city driving.

Table 10. Average properties of airborne particulate matter and tunnel wall deposits collected at the Detroit & Canada Tunnel, 15 June-10 July 1973

	Tunnel exhaust			
	River	Land	Intake	Wall
Pb	6.8%	6.6%	1.3%	0.35%
Zn	0.22%	0.24%	0.25%	0.24%
C[a]	31%	30%	18.7%	18.8%
Residue after O_2 + oCl$_2$Ø extract	79%	76%	78%	80%
Specific surface area	$4.5\frac{m^2}{g}$	$5.0\frac{m^2}{g}$	$3.1\frac{m^2}{g}$	$0.45\frac{m^2}{g}$
after O_2 + oCl$_2$Ø extract	$44.9\frac{m^2}{g}$	$39.2\frac{m^2}{g}$	$11.2\frac{m^2}{g}$	$9.1\frac{m^2}{g}$
SBR (total all extracts)	0.71%	0.61%	0.26%	2.4%

[a] Total carbon, free and combined.

Experiment 6/15/73

Air samples were collected in the exhaust chimneys and intake fan room continuously over the period June 15 through July 10, 1973. At each station there were 47-mm and 142-mm diameter membrane filters, pore size 0.2μ oriented with collection surfaces downward. In the chimneys the filters were centered about 2 meters below the top; baffling to exclude large particles consisted of only a single disk over the holder opening. In the intake fan room the membrane filters were elaborately baffled. The intake air was sampled throughout with a standard Hi-vol unit equipped with 8" x 10" glass fiber filters. Material deposited on the tunnel walls was also sampled.

Properties of the materials collected are listed in table 10. Infrared spectra (for example, figures 8,9,10) show SBR in all samples. Recalling the average SBR content of tire tread, we see that 1 percent of the suspended particulate loading in the Detroit ambient air sampled was tire debris.

Table 11. Aerosol concentrations at Detroit and Canada Tunnel, experiment 15 June 1973

	Average concentration, $\mu g/m^3$					
					SBR	
	Gross	Pb	Zn	C	C_6H_6 extract	$\Sigma(O_2 + oCl_2\phi)$ extracts
River section						
6/15-6/28	319	16.7	0.675	109	0.80	1.62
6/28-7/10	321	24.3	0.637	100	0.41	0.94
Land section						
6/15-6/28	208	10.8	0.577	60	0.38	0.88
6/28-7/10	236	18.8	0.476	75	0.35	0.50
intake fan room						
6/15-6/21[a]	101	1.16	0.284	20.2	0.136	0.149
6/21-6/28[a]	90	1.06	0.199	18.3	0.131	0.110
6/28-7/5[a]	111	1.79	0.279	21.2	0.169	0.224
7/5-7/10[a]	157	1.62	0.310	--	0.194	0.203
6/15-7/10 membrane[b]	103	--	--	--	0.077	0.138

Intake SBR/Pb = 0.18 to 0.23 (average = 0.21)

[a] Hi-vol and 47 mm membrane filters.

[b] 142 mm membrane filter.

Standard-addition experiments indicated essentially quantitative SBR recovery in all cases. Many $oCl_2\phi$ extractions, however, were required to remove all the SBR from the wall sample, which appears (table 10) to have a tire-debris content of approximately 10 percent.

Table 11 shows the airborne concentrations of species of interest obtained in this experiment. The Hi-vols generally gave about 13 percent higher gross concentrations than the membranes. The 47- and 142-mm membranes agree better.

Earlier Experiments

Atmospheric concentrations measured in previous experiments at the Detroit & Canada Tunnel are listed in table 12. The main differences from the 6/15/73 experiment were that the earlier experiments (a) included some sampling in the ducts, (b) had less effort to exclude larger particles, and (c) had poorer sensitivity (related to sample size and analytical procedures).

The 4/10/70 experiment serves to indicate the extent of losses of suspended particulate matter from the air stream as it moves through the system. Comparing the loadings at the inlet fan room and in the inlet duct, one sees little evidence for significant losses, other than possibly of Pb, in the intake system. There seems to be a decrease in gross particulates between the outlet duct and exhaust chimney, which is expected since most of the particulate matter generated by traffic is settleable judging by the experience in the Allegheny Tunnel (table 9); otherwise there seems to be no significant loss occurring in the exhaust system.

Table 13 shows the relative concentrations of airborne particulate matter generated within the Detroit & Canada Tunnel during all experiments, obtained by subtracting the respective intake concentrations. The first and last columns indicate that 2 percent to 4 percent is tire debris (½ percent to 1 percent is SBR).

With the subtraction of 0.006 from the $\Delta Zn/\Delta Pb$ ratio to account for the contribution of engine lubricant, the residual ratio ranges between zero and 0.14 (average 0.026). The lowest ratios occur at the same time of year in 1971 and 1973, and the 1973 ratio has low SBR values to support it. The time happens to embrace two major holidays (one U.S., one Canadian) in each case, and the Pb values themselves are high. Probably traffic congestion in the tunnel is the explanation.

EXPERIMENTS AT ROTUNDA DRIVE, DEARBORN

The site is a sharp curve (radius of curvature about 64 meters, length about 81 meters) in Rotunda Drive at the edge of the Ford Engineering Center in Dearborn, Michigan. The setting is suburban. Rotunda Drive is an asphalt-surfaced four-lane artery about 19 meters wide carrying moderate traffic, predominantly automobiles. There are curve warning signs suggesting

Table 12. Earlier aerosol measurements at the Detroit and Canada Tunnel

	Average concentration, $\mu g/m^3$			
	Gross	Pb	Br	Zn
3/4/70 River section				
Outlet duct	666	57	31.9	2.2
Intake duct	148	3.2	0.9	0.49
3/5/70 River section				
Outlet duct	864	26	12.9	0.96
Intake duct	34	3.0	1.2	0.66
4/10/70 River section[a]				
Exhaust chimney	2019	52	22.1	2.9
Intake fan room	165	8	1.5	0.28
Outlet duct	2386	52	24.4	3.0
Intake duct	174	4	1.4	0.26
6/28/71-6/30/71 River section				
Exhaust chimney	337	21.1		3.41
Intake fan room	134	1.5		0.52
6/30/71-7/4/71 River section				
Exhaust chimney[b]	206	28.1		0.265
Intake fan room	74	2.0		0.158
7/7/71-7/12/71 Land section				
Exhaust chimney[c]	249	27.2		0.497
Intake fan room	118	2.1		0.298

[a] No trucks (Teamsters strike).

[b] SBR presence was also established, by an infrared method now known (ref. 6) to lead to losses: C_6H_6 extract = 0.31 $\mu g/m^3$, $(O_2 + oC\ell_2\phi)$ extract = 0.51 $\mu g/m^3$.

[c] SBR presence was also established, $(O_2 + oCl_2\emptyset)$ extract = 0.38 $\mu g/m^3$ (but see preceding footnote).

Table 13. Relative amounts of airborne particulate species generated inside the Detroit and Canada Tunnel

	Outlet minus intake, $\mu g/m^3$					
	ΔGross	ΔPb	ΔBr	ΔZn	ΔC	ΔSBR
3/4/70 River	518	54	31	1.7		
3/5/70 River	830	23	11.7	0.30		
4/10/70 River[a,b]	2033	46	22	2.7		
6/28-6/30/71 River	203	19.6		2.9		
6/30-7/4/71 River	132	26.1		0.11		
7/7-7/12/71 Land	131	25.1		0.20		
6/15-6/21/73 River	177	21.0		0.388	92	2.19
6/21-6/28/73 River	233	11.0		0.479		
6/28-7/5/73 River	175	23.8		0.287	(79)[c]	1.00
7/5-7/10/73 River	184	21.2		0.416		
6/15-6/21/73 Land	64	9.7		0.312	43	1.03
6/21-6/28/73 Land	176	9.7		0.357		
6/28-7/5/73 Land	126	17.0		0.182	(54)[c]	0.49
7/5-7/10/73 Land	96	17.1		0.187		

[a] Average of chimney minus fan room and outlet duct minus intake duct.

[b] No trucks (Teamsters strike).

[c] Approximate; carbon loading at intake during the interval 5-10 July 1973 was not measured.

slowing to 30 mi/hr from the posted 40 mi/hr speed limit. The suggested speed is frequently exceeded, and the wear on tires is undoubtedly severe; at the speed limit, the centrifugal acceleration would be about 325 cm/second^2, which should correspond (ref. 46) to a wear rate of some 1 to 6 mils per mile, or 7 to 40 grams per mile per tire. At that rate, a tire would last only a few hundred miles.

Stop-and-go traffic prevails at this site for about 20 minutes each weekday. This, together with occasional idling on nearby side streets, operation of off-road vehicles, occasional testing of engines by Engineering Center personnel, and the incessant gasoline-powered lawnmowers in season, will probably contribute a small amount of spurious exhaust particulates with a commensurate overestimate of the relative importance of the latter.

Sample Collection. The disposition of the sampling site and apparatus is shown in figure 11. Samples were collected on 47- and 142-mm diameter membrane filters (mean pore flow diameter 0.2μ) and on standard Hi-vol samplers equipped with 8" x 10" glass or quartz fiber filters. Glass and quartz filters run concurrently on two Hi-vols showed no difference in their SBR results.

The membrane filters were extensively baffled to exclude large particles and installed in the weather shelters, collection surfaces downward. Running times were of the order of 5 days for the Hi-vols, and weeks for the membranes. Soil samples (about 7 cm diameter × 5 cm deep) and dustfall samples were also collected. The airborne SBR size distribution was obtained with a standard Hi-vol cascade impactor with glass-fiber-filter collection surfaces.

Results. SBR was found in all air samples, in dustfall, and in soil (figures 12,13,14). Properties of the aerosol are listed in table 14. The SBR/Pb ratios indicate that the generation of airborne tire debris here is substantial. The SBR in the dustfall was 1.44 percent (indicating some 6 percent tire debris which may be compared with the value ~2 percent reported by Cardina (ref. 4) near traffic).

The Hi-vols usually collected substantially more material, on a μg/m^3 basis, than did the membranes. We attribute this to the better shielding of the latter against large particles. The bias for greater SBR collection in the Hi-vols was about the same as that for the gross particulates, hence the agreement between membrane and Hi-vol SBR calculated as a percentage of gross mass. Supporting further the large-particle hypothesis is the observation that a Hi-vol without the motor running collected 2-4 percent as much SBR and 2.6 percent as much gross particulate--clearly not aerosol--as a running, but otherwise identical, Hi-vol next to it. The lowest mass loading and the next-lowest SBR was observed in a sampling period 3/9-3/15/73 during which there occurred an exceptionally severe snowstorm which covered everything for many days. In general, the SBR concentration measured by the Hi-vols goes up when the total particulate loading does (figure 15), as would be expected if, for example, resuspension of dust by wind were a controlling factor.

The size distribution of the airborne SBR (figure 16), the relatively high SBR in the dustfall, the amount of SBR in the soil and its rapid decline with distance away from the road (figure 17; the half-distance is about 1 to 2 meters), and finally the higher SBR values obtained for the Hi-vols relative to the membrane filters, all point to the predominance of large particles. Extrapolation of figure 17 suggests that most of the SBR particles settle initially onto the roadway itself. A reveiw of the literature concerning tire-wear mechanisms would lead one to expect that particles produced by severe wear should be large (ref. 15), in accord with our evidence.

As at Allegheny Tunnel, a settling tendency that is greater for SBR than for Pb particles is observed (compare SBR/Pb ratios in the air and at the edge of the road, table 14 and figure 17).

At the high-speed turn in the Ford test track in Dearborn, the SBR concentration in the soil varies with distance from the road, qualitatively like that at Rotunda Drive, but on a longer distance scale (figure 18; the asymmetry between the inside and outside of the curve may be wind-induced).

Standard-addition experiments show high SBR recoveries in the aerosol and dustfall samples. Appropriate corrections were made. Sometimes significant losses occurred in the soil and impactor-stage samples at the lower concentrations. We do not attempt to correct for this, and therefore

Table 14. Properties of the aerosol at Rotunda Drive

	Collected by membrane	Collected by Hi-vol
Total mass, $\mu g/m^3$	59.3 (33-109)	107 (35-271)
Pb	1.53 (0.62-3.5) $\mu g/m^3$ = 2.67 (1.30-4.7)%	
Zn	0.21 (0.13-0.35) $\mu g/m^3$ = 0.37 (0.20-0.52)%	
C[a]	6-12 $\mu g/m^3$ = 15-23%	
Residue after C_6H_6 extraction	84%	
after O_2 + oCl_2Ø extraction	73-77%	
Specific surface, initial	1-3 m^2/g	
after C_6H_6 extraction	6 m^2/g	
after O_2 + oCl_2Ø extraction	12-25 m^2/g	
SBR (total all extracts)	0.34 (0.23-0.41) $\mu g/m^3$ = 0.60 (0.50-0.73)%	0.54 (0.17-1.5) $\mu g/m^3$ = 0.54 (0.22-1.2)%
% SBR/% Pb	0.30 (0.23-0.38)	0.32 (0.21-0.42)

[a] Total carbon, free and combined.

the SBR soil concentrations may actually be somewhat higher than shown in figures 17 and 18.

ERRORS AND INTERFERENCES

Zinc. The importance of extraneous sources of Zn is obvious from some of the data. Only in the wall deposits and dustfall in the tunnels, and in the walkway gutter deposit at Allegheny, can tire debris account for as much as half of the Zn, according to Zn/SBR ratios (tables 3,8,10). The sporadic behavior of Zn concentrations at the Detroit & Canada Tunnel and the high $\Delta Zn/\Delta Pb$ ratios there would probably be unattainable if tire wear were the only Zn source. The tunnel-air $\Delta Zn/\Delta Pb$ ratios are in turn so much lower than the atmospheric Zn/Pb ratios that it is evident that tires are not a major source of atmospheric Zn.

One source which impairs the value of Zn as a tracer even in the tunnels is engine exhaust. The estimated amount of motor-oil Zn from gasoline-engine exhaust alone is comparable to, and sometimes higher than, the total Zn observed in the air of the tunnels. This estimate itself is uncertain and should be regarded with reservation.

The Zn content of tire debris is assumed to be the same as in the parent material. Agglomerations rich in Zn and up to 30μ in diameter sometimes form in tire tread material (refs. 47,48,49), and hence some segregation by preferential settling is conceivable. To the extent that vaporization of any other tread constituent occurs, the Zn found will exaggerate the amount of tire particulate matter present, but will serve instead to indicate the total amount of airborne tire debris, both gaseous and particulate.

SBR. The main concern with SBR is oxidation. This is probably not a source of error in the tunnels. The open atmosphere is another matter. Ozone attack would seem a certainty. Photochemical decomposition (by ultraviolet light) and oxygen attack (refs. 50,51,52,21) can be expected to occur in the daytime. Proximity of the sampling site to the source (as at Rotunda Drive) might ameliorate the problem, but one must recognize that the SBR found by infrared spectroscopy might underestimate the amount of particulate tire debris actually present in the case of the open-air samples.

Decomposition during the wear process itself (thermal decomposition) is probably not serious. Thermogravimetric analysis of decomposition of the standard E249-66 tread vulcanizate in air shows that temperatures at the contact points between tire and roadway would have to reach ~380°C before the induction time for decomposition would be as short as the reaction time available ($\sim 10^{-2}$ seconds in the footprint, per revolution). The material balance in SBR at the Allegheny Tunnel also argues against decomposition errors.

Some deterioration with the passage of time is known to occur in at least some air samples, namely, Hi-vol samples collected from the Detroit air during the Detroit & Canada Tunnel 6/15/73 experiment. Portions extracted promptly after collection and duplicate portions extracted after 6 months' storage in the dark at room temperature showed good agreement in the $oCl_2\phi$ extracts, but the benzene extract of the stored sample showed 40 percent less SBR than was found in the earlier-extracted duplicate.

Overestimate of the amount of SBR seems unlikely. Some 65 percent of the U.S. production of SBR during 1969-1971 was utilized in tires (refs. 25, 26,27); hence, the possibility of the influence of nontire SBR sources is remote. Other substances can contribute to the lines in the SBR infrared spectrum at 10.35μ (trans-olefins) and 14.3μ (monosubstituted aromatic compounds). We have mentioned polybutadiene (olefinic linkages). Gasoline contains 1,3 pentadiene and other olefins. In automobile exhaust particulate samples we have measured a 10.35-μ absorption equivalent to 0.2 percent rubber in benzene extracts and <0.1 percent rubber in $oCl_2\phi$ extracts. Samples of Diesel-exhaust particulate extracted first with benzene and then with $oCl_2\phi$ showed weak 10.35-μ absorption in the latter. Linnell and Scott (ref. 53) found no 10.35-μ absorption in Diesel exhaust particulate. Asphalt samples did not give the SBR spectrum.

Interfering compounds would probably appear primarily in the benzene extracts. Fortunately, we find most (average about 65 percent) of the SBR in the $oCl_2\phi$ extracts, where, moreover, the likelihood of interferences is easily gauged by comparing the 10.35/14.3-μ intensity ratio with that for SBR.

Absence of lines at 10.35 and 14.3μ in the Allegheny Tunnel intake-air samples argues against presence of natural sources that might interfere in air samples generally.

Gel permeation chromatography was performed on a sample collected in a Hi-vol filter displaying a strong SBR infrared spectrum in the oCl$_2\phi$ extract. An aliquot of this extract was passed through the GPC column. At the point in the elution where SBR comes off the column, the effluent was trapped. Its infrared spectrum proved to be that of SBR. The amount of SBR in the trapped stream as calculated from the spectral intensities agreed with the amount present before injection onto the column. This indicates that we were dealing with one species, having the same infrared spectrum as SBR and approximately the same molecular weight as SBR.

COMPARISON OF TIRE AND EXHAUST PARTICULATES

We wish to compare the amount of airborne tire particulates, from vehicles of all types, against the amount of airborne exhaust particulates from automobiles and other gasoline-powered vehicles.

The Pb content of airborne automobile exhaust particulate matter is variously reported as 12 to 74 percent (refs. 54-68). Our measurements at the Detroit & Canada Tunnel 6/30-7/4/71 and 7/7-7/12/71 show that the number is $\geq$20 percent. We adopt 40 percent as the value, as found by Mueller *et al.* (refs. 62,63,64) at 60 mi/hr. Choice of a lower value would result in lower estimates for the amount of tire particulates relative to exhaust.

The foregoing, together with 25 percent and 1.0 percent for the average SBR and Zn contents, respectively, of tread rubber as already discussed, give relative amounts of airborne tire debris and gasoline-engine exhaust particulate shown in table 15. The sites are arranged in approximate order of increasing severity, from high speed cruise through urban driving to cornering. A reasonable estimate at a nationwide average might be 0.2 on the basis of this table.

Larson and Konopinski (ref. 18) found $\Delta Zn/\Delta Pb = 0.0167$ in Boston's Sumner Tunnel, similar to the values obtained in our tunnel experiments. With the (0.006) correction for the Zn contributed by lubricating oil, their result implies <0.43 as the maximum ratio between tire particulates and gasoline-engine exhaust particulates at that tunnel.

Our SBR/Pb ratios at all sites taken together indicate that tire-

Table 15. Mass ratios between airborne tire particulate and airborne gasoline-engine exhaust particulate

	Particulate mass ratios calculated from Zn/Pb	Particulate mass ratios calculated from SBR/Pb
Allegheny Tunnel		
Eastbound	<0.30[a]	0.035-0.11
Westbound	<0.27[a]	--
Allegheny Mountain ambient (intake fans)		0(<0.2)
Detroit and Canada Tunnel		
U.S. River section	<0.7[a,b]	0.22[d]
U.S. Land section	<0.5[a,c]	0.17[d]
Detroit ambient (intake fans)		0.33
Rotunda Drive		0.50

[a] From average Zn/Pb ratios with contribution of gasoline-engine exhaust-particulate Zn (Zn/Pb = 0.006) subtracted out.

[b] Minimum Zn/Pb at this site, with motor-oil correction applied, would give $\frac{\text{tire particulates}}{\text{gasoline-engine exhaust particulates}} = \text{zero}$.

[c] Minimum Zn/Pb at this site, with motor-oil correction applied, would give $\frac{\text{tire particulates}}{\text{gasoline-engine exhaust particulates}} = 0.08$.

[d] Data for the period of 15-28 June 1973 only. SBR/Pb ratios for the period of 28 June to 10 July 1973 are believed to be anomalously low because of traffic jams in the tunnel.

particulate levels in urban atmospheres should be generally on the order of 0.5 to 1 $\mu g/m^3$, or 1 percent of the gross airborne particulate loading, i.e., comparable to (say, one half of) current atmospheric Pb levels. This agrees with our measurements of the Detroit air (see tables 10,11).

If the rate of generation of airborne Pb particulates per mile from gasoline-engine exhaust is of the same order at the other sites as it was at the Allegheny Tunnel (and at the Sumner Tunnel), our SBR/Pb ratios imply airborne tire-particulate generation rates around 0.004 grams per mile per tire in the Detroit & Canada Tunnel, 0.006 in Detroit, and 0.009 at Rotunda Drive--or, from wear estimates previously given, airborne tire-particulate generation rates of ~2 percent of the total wear rate in the Detroit & Canada Tunnel, ~3 percent in Detroit, and 0.02-0.1 percent at Rotunda Drive. We have seen that the figure was 2 to 7 percent at the Allegheny Tunnel. Thus, though the amount of airborne tire particulate on a gram/mile basis increases with increasing severity of wear, it probably remains a relatively constant fraction (~5 percent) of the total wear.

SUMMARY

We conclude that:

1) Airborne particulate matter from rubber tires is present in minor amounts in the atmosphere;

2) This airborne particulate constitutes a small fraction of the total tire wear--perhaps 5 to 10 percent on the average;

3) Most of the rest exists in the form of nonsuspendable particles deposited near the road;

4) Tire debris comprises a small fraction (perhaps 1 to 4 percent) of the total airborne particulate matter generated by road vehicles of all categories in tunnels;

5) Depending on driving conditions, the amount of airborne tire particulate matter is ~20 percent as great as the amount of airborne exhaust particulate matter from gasoline engines burning leaded fuel (from ~5 percent under mild-wear conditions to 45 percent under severe conditions);

6) The concentration of airborne tire particulate matter in urban

areas is probably of the order of 1 μg/m^3 or 1 percent of the total particulate loading.

Item (2), as well as (5), suggests that the nationwide production of airborne tire particulates would not justify considering tire wear a major source of air pollution. We have to stop short of dismissing it altogether, for we lack detailed knowledge of the chemistry of the small amount that does go into the atmosphere. No concrete roadways have been explicitly examined in our study, and one may ask if they might differ from asphalt in a pertinent way. At the moment, however, the possibility of showing airborne tire particulates as a major air pollution problem seems remote.

Evidence of silica or silicate was occasionally noted in tunnel outlet air, suggesting a role that mineral debris might play in the particulates generated by vehicles. This prompts mention of the work of Thelin (ref. 69), who rubbed a vulcanizate sample over a brass plate strewn with abrasive particles that were free to roll (as in a roadway situation, and not as in a laboratory tire test where the abrasive is fixed to the "road" surface) and found that much more brass than rubber was abraded. It would therefore seem pertinent to test the hypothesis that the important material resulting from tire wear may be abraded from the roadway rather than from the tire.

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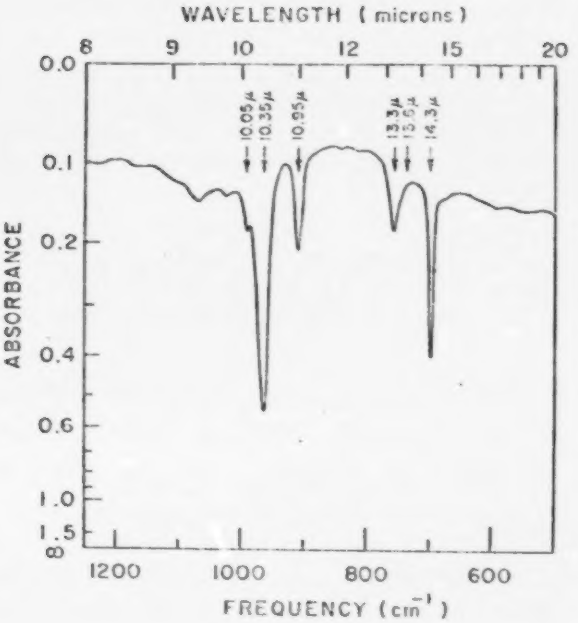


Figure 1. Infrared spectrum of SBR-1500. The lines at 13.3 and 14.3μ are from the aromatic rings of the styrene units of the copolymer chain. The other four indicated lines (one of which cannot be seen in this spectrum) are associated with butadiene units; of these four, the strong one at 10.35μ is associated with 1,4 addition in a trans configuration, the unobserved one at 13.6μ is associated with 1,4 addition in a cis configuration, and those at 10.05 and 10.95μ are associated with 1,2 addition. It can be seen that there is little of the cis configuration in this material.

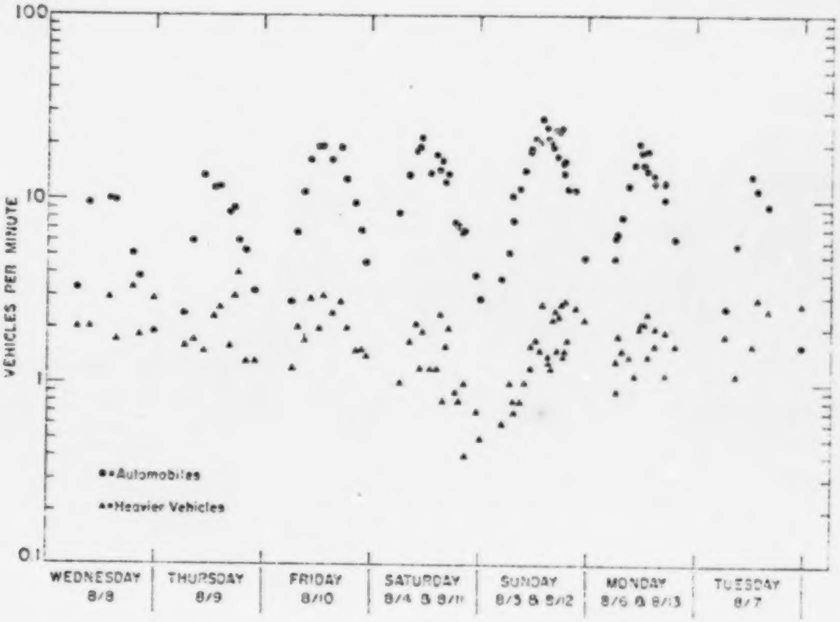


Figure 2. Visual counts of eastbound traffic, by categories, in the Allegheny Tunnel during the 8/1/73 experiment. In the "Heavier Vehicles" category, about 72 percent are Diesel-powered.

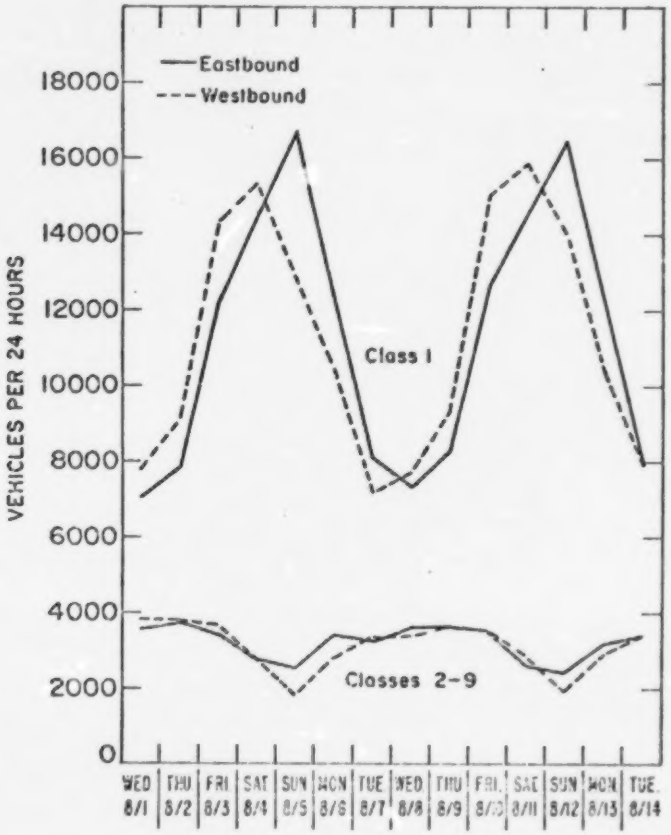


Figure 3. Eastbound (solid lines) and westbound (dashed lines) 24-hour traffic totals at Allegheny Tunnel during the 8/1/73 experiment. Class 1 consists of light vehicles, primarily automobiles, and Class 2-9 consists of heavier vehicles (trucks and buses).

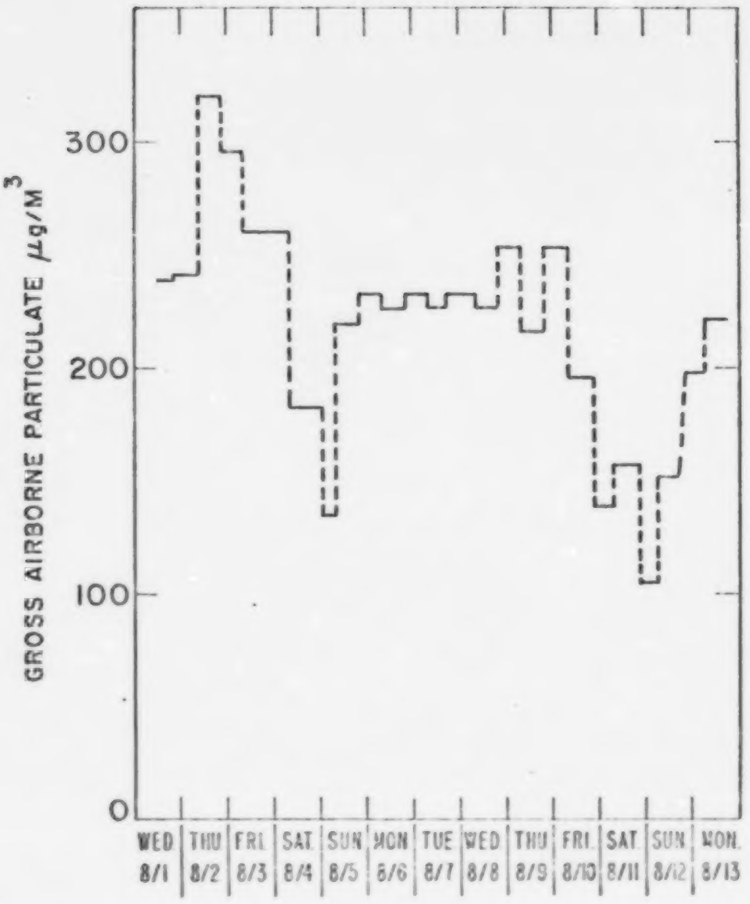


Figure 4. Gross airborne particulate loadings at Allegheny Tunnel East Portal, eastbound tube, during the period 8/1/73 to 8/13/73, Hi-vol samples.

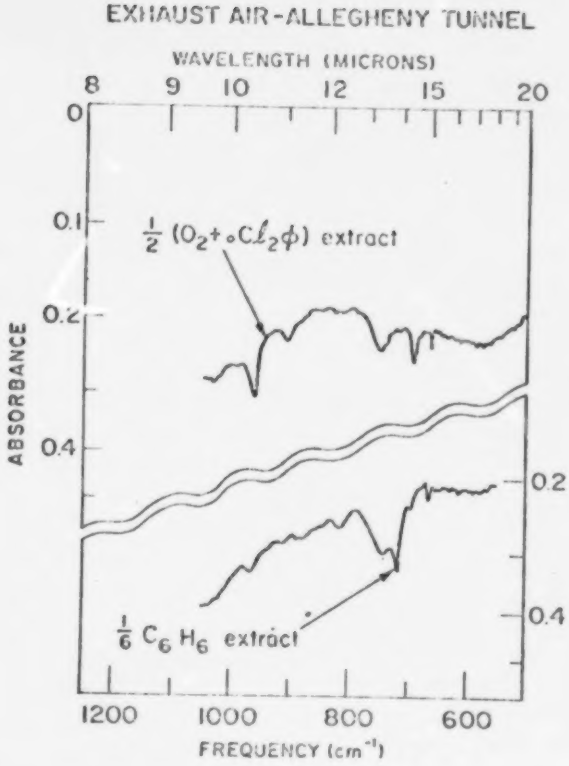


Figure 5. Infrared spectra of benzene and $oCl_2\phi$ extracts of aerosol in the Allegheny Tunnel 8/1/73 experiment. These are from a Hi-vol sample collected 0640-1912 EDT Sunday 12 August at the East Portal station in the eastbound tube. As indicated, the spectra correspond to 1/6 of the benzene extract and 1/2 of the $oCl_2\phi$ extract (from one half of the filter).

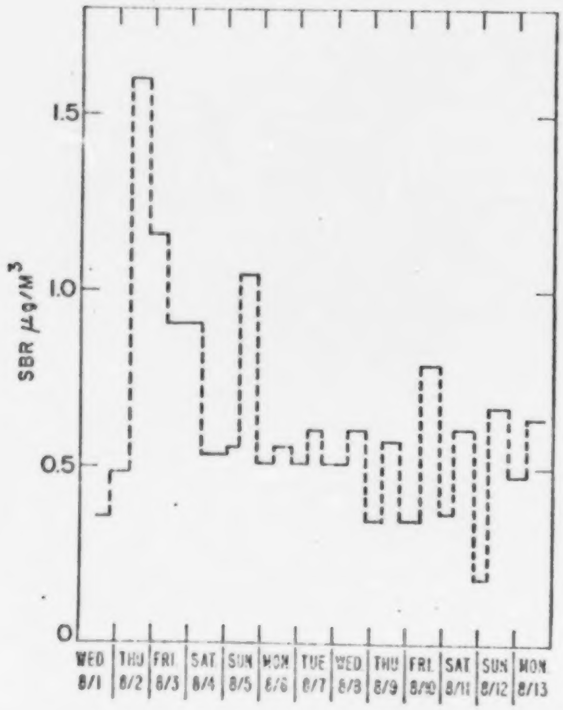


Figure 6. Airborne SBR concentrations at Allegheny Tunnel East Portal during the period 8/1/73 to 8/13/73, Hi-vol samples.

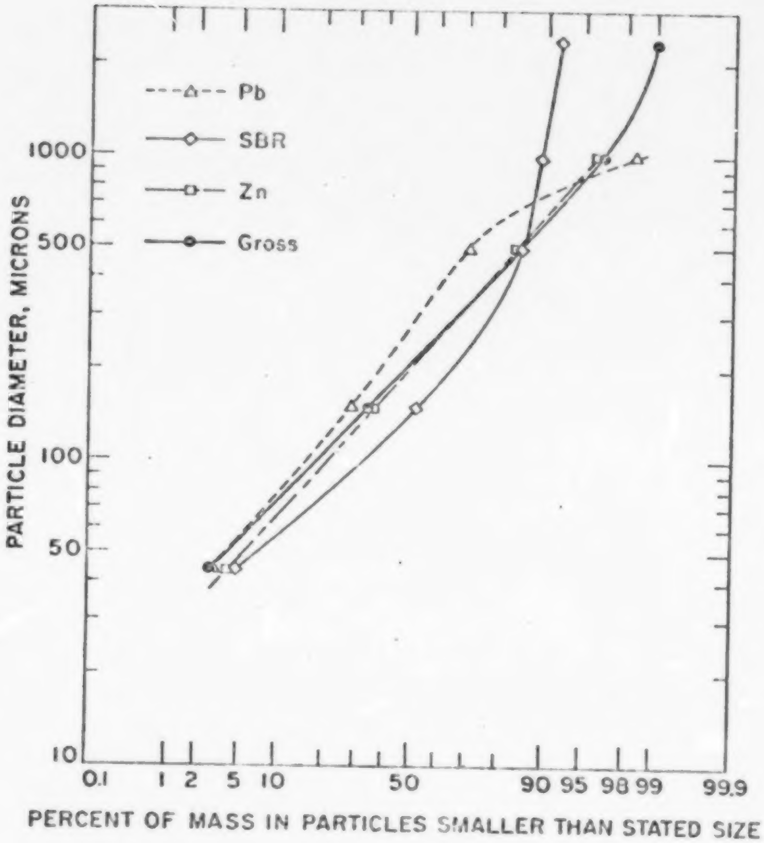


Figure 7. Size distributions of gross mass, Pb, Zn, and SBR in the roadway gutters of the Allegheny Tunnel, eastbound tube, right-hand lane, near the East Portal.

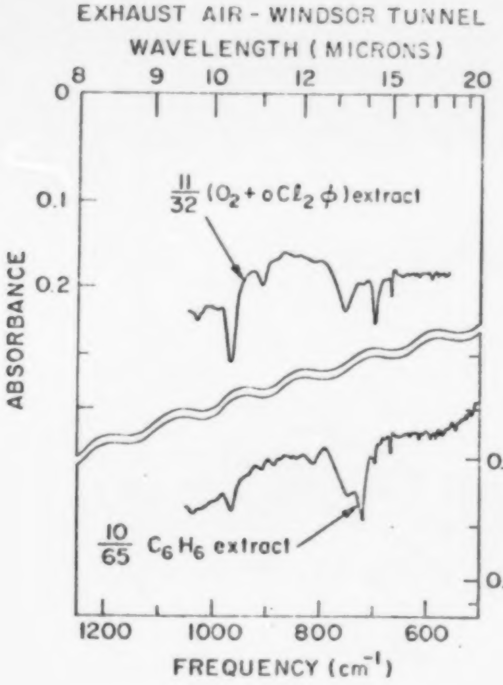


Figure 8. Infrared spectra of benzene and $oCl_2\phi$ extracts of aerosol in the Detroit & Canada Tunnel. These are from a membrane-filter sample collected from 1435 EDT 15 June through 1055 EDT 28 June 1973, in the exhaust chimney for the U. S. River section.

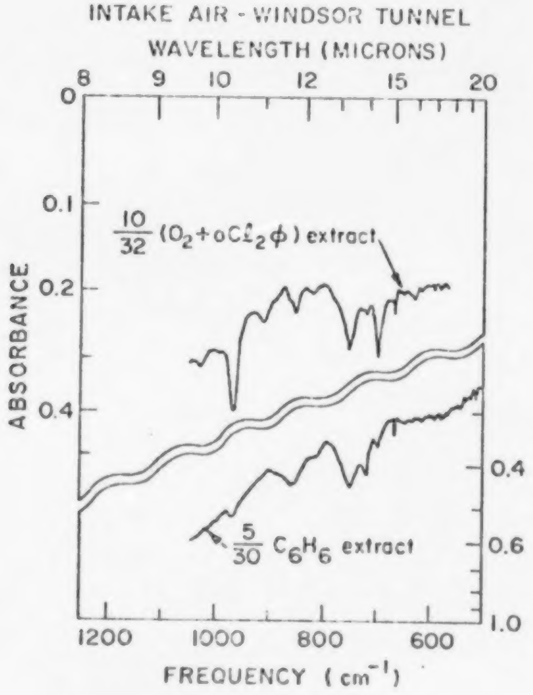


Figure 9. Infrared spectra of benzene and $oCl_2\phi$ extracts of aerosol at the ambient-air intake of the Detroit & Canada Tunnel. These are from a Hi-vol sample collected from 1304 EDT Thursday 28 June through 0938 EDT Thursday 5 July 1973.

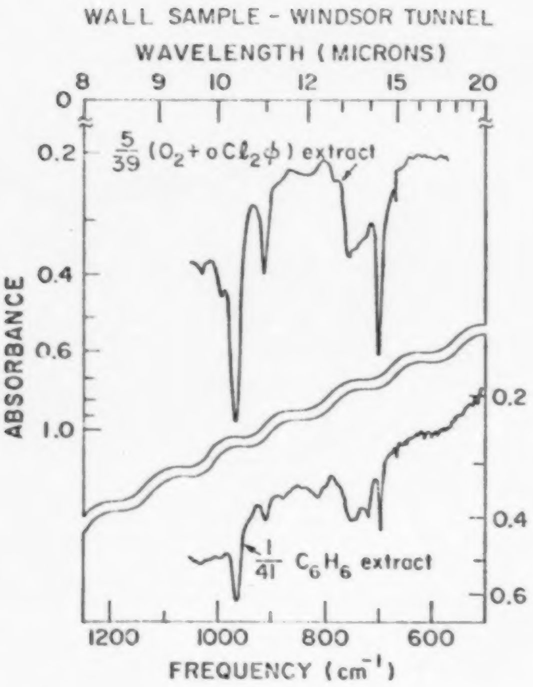
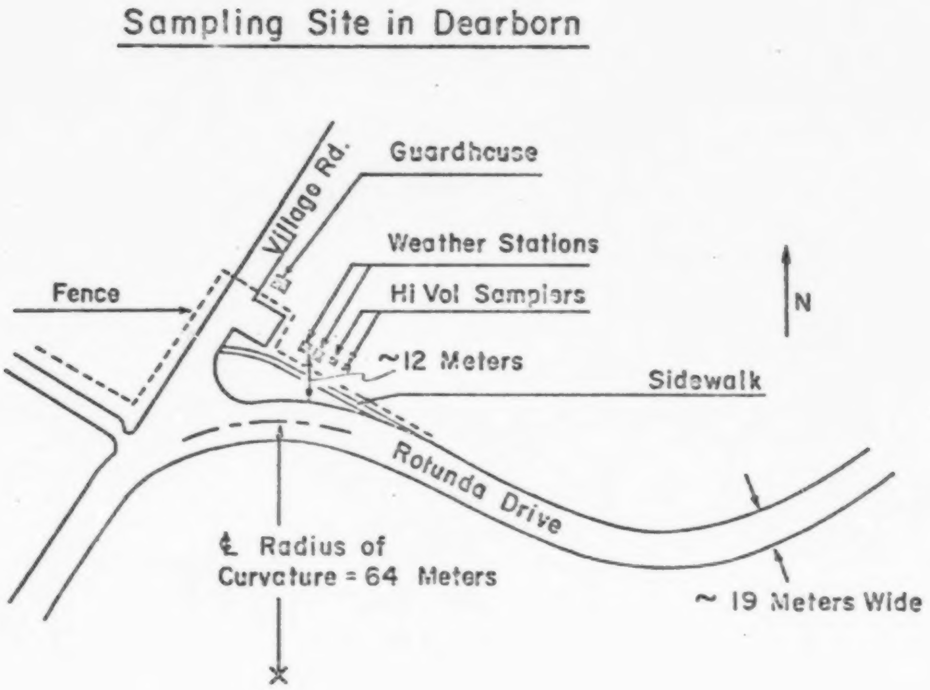

WALL SAMPLE - WINDSOR TUNNEL

Figure 10. Infrared spectra of benzene and $oCl_2\phi$ extracts of dirt adhering to the wall of the Detroit & Canada Tunnel. This sample was collected from a spot 160 meters into the tunnel from the U.S. end.



Sampling Site in Dearborn
Village Rd.
Guardhouse
Weather Stations
Fence
Hi Vol Samplers
N
~12 Meters
Sidewalk
Rotunda Drive
℄ Radius of
Curvature = 64 Meters
~ 19 Meters Wide

Figure 11. Rotunda Drive sampling site, Dearborn, Michigan.

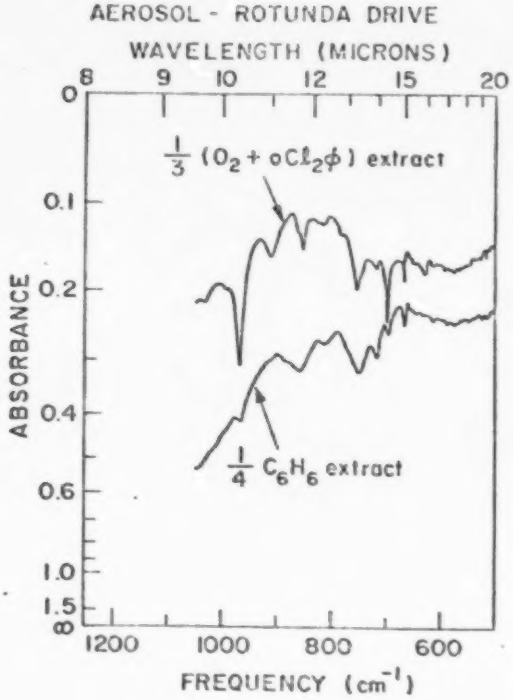


Figure 12. Infrared spectra of benzene and $oCl_2\phi$ extracts of aerosol at Rotunda Drive. These are from a Hi-vol sample collected 1517 EST 23 April to 1509 EDT 30 April 1973.

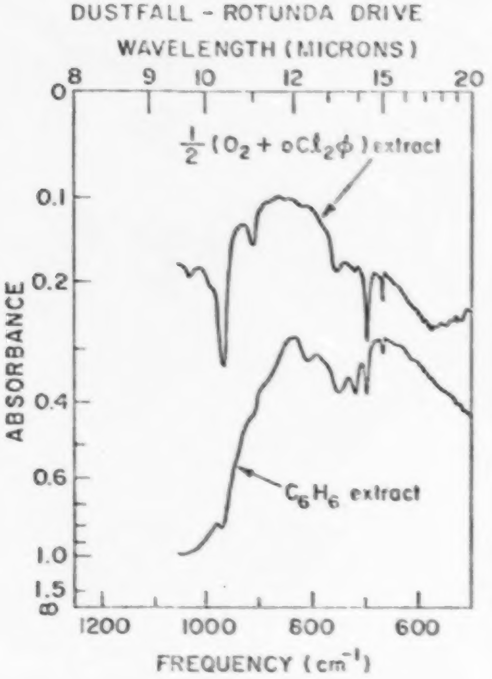


Figure 13. Infrared spectra of benzene and $oCl_2\phi$ extracts of dustfall 12 meters from the roadway at Rotunda Drive. This sample was accumulated over the period of 21 March to 30 April 1973.

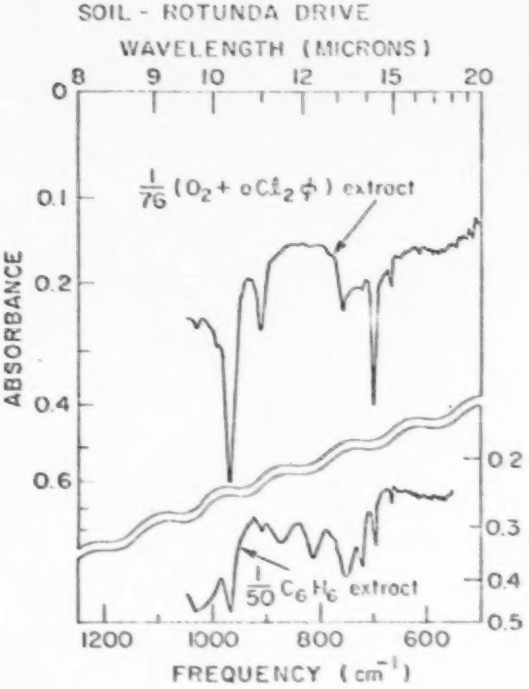


Figure 14. Infrared spectra of benzene and $oCl_2\phi$ extracts of soil at Rotunda Drive. This was 20 grams from soil collected 1 meter from the roadway 5 May 1973.

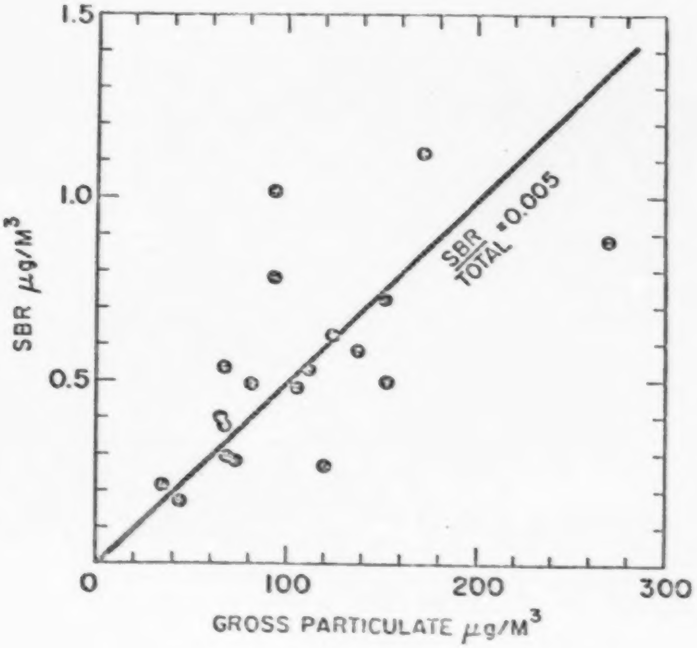


Figure 15. Airborne SBR vs. total particulate concentrations at Rotunda Drive. Line is drawn by eye (not a least-squares fit).

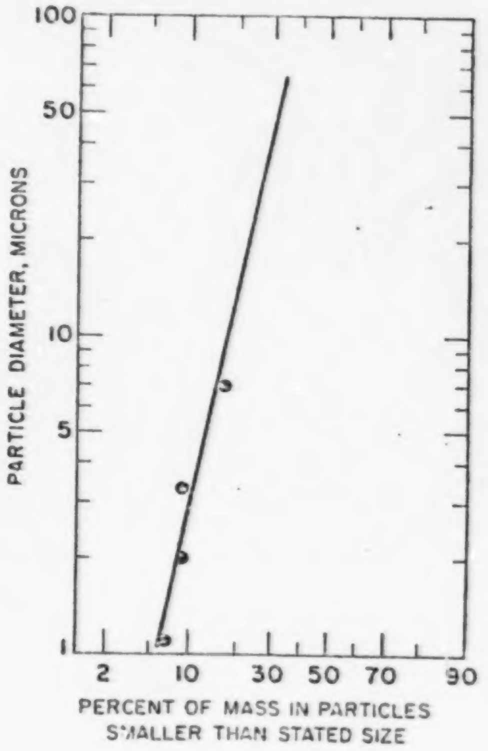


Figure 16. Size distribution of airborne SBR at Rotunda Drive. Notice that the curve extrapolates to a mass mean diameter larger than 20μ (aerodynamic diameter, $\rho^{1/2}d$).

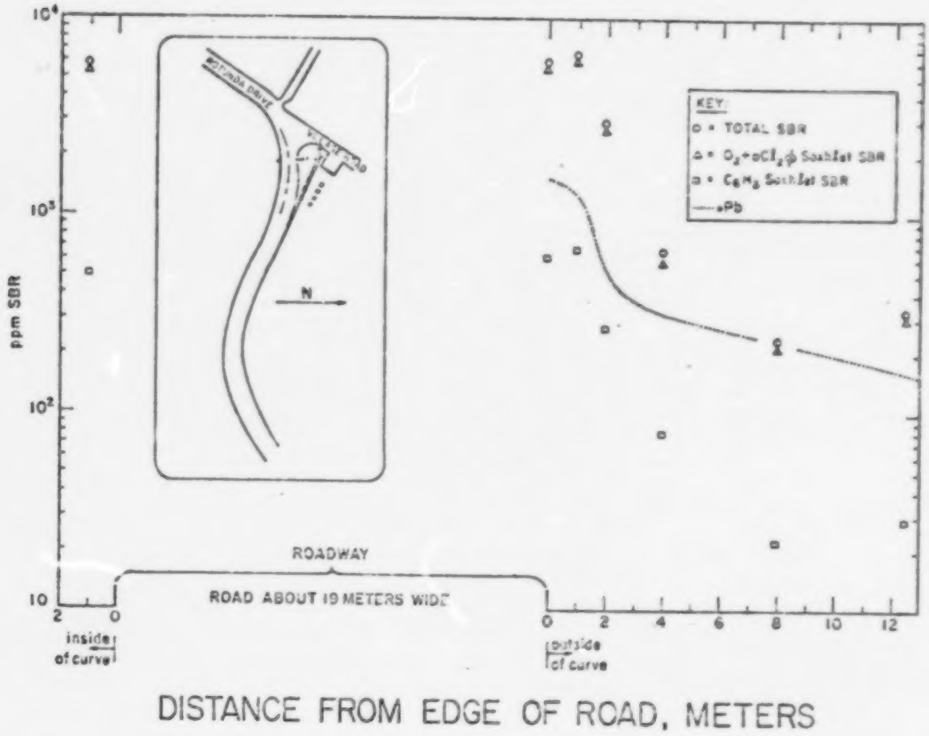


Figure 17. SBR soil concentrations at various distances from the roadway at Rotunda Drive. Dots on the inset, on a line normal to the roadway, show the spots where the samples were taken. The point 12-1/2 meters from the outside of the curve is next to a paved turnaround area and probably should be ignored; SBR was 20 ppm in soil 185 meters from the road. Dotted curve shows Pb concentrations.

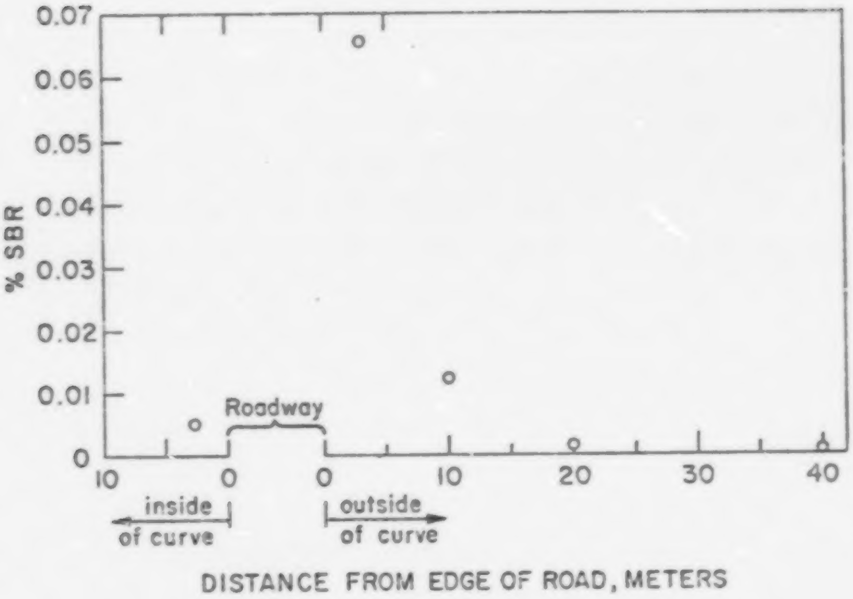


Figure 18. SBR content of roadside topsoil 11/10/71 at various distances from the high-speed "flat turn" of the Ford Motor Company test track, Dearborn Proving Ground. Determined by infrared spectra. Sum of SBR in benzene and $oCl_2\phi$ extractions.

RUBBER DUST FROM THE NORMAL WEAR OF TIRES

Mark L. Dannis*

Abstract

Tires wear out in normal use. Tread-rubber losses have been studied to find out if the rubber abrades to particles, degrades to an intermediate state, or oxidizes to volatile vapors and gases. Particulate erosion seems to be the dominant mechanism.

Particles worn from tires were first collected on sticky panels mounted under the car. The particles are not spherical, but approach cylinders or sausage shapes as a limit. An isokinetic filter system was later developed. The particles caught on filter plates were examined, transferred to microscope slides, photographed, then counted to obtain particle size distributions. Smooth distributions were obtained, linear on logarithm of volume, cumulative probability graphs. The geometric mean particle size is about 20μm equivalent diameter.

Special effort was devoted to a search for very small particles, from about 1/2 to 3μm equivalent diameter. This is the diminishing tail on the distribution curve. Very few of these particles could be found.

Attempts were made to identify volatile emission from a running tire, using chromatographic techniques and a flame ionization detector without success. Particular erosion seems to be the dominant loss mechanism.

Tire dust particles have a high specific surface and are subject to oxidation. Simple chemical oxidation is slow, but biochemical oxidation at the soil surface under the combined influence of oxygen, photoexcitation, and enzyme catalysis can be rapid, returning the carbon content to the normal biological carbon cycle.

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*Research Fellow, Research and Development Center, The B. F. Goodrich Company, Brecksville, Ohio 44141.

INTRODUCTION

Background

Automobile and truck tires wear out. Recent reviews by Clark (ref. 1), Schallamach (ref. 2), and others point out that frictional wear and traction always accompany one another, but the relationship is affected by the compounding of the rubber, the construction of the carcass, the nature of the road surface, the speed of the car, and other factors.

Very little has been published on the debris worn off the tire. Tire debris is seldom visible during erosion or visible as accumulation on the road. A few attempts have been made to look for tire wear products in constricted traffic locations, such as tunnels, where the ventilation system offers a convenient collection and concentration system. Worn rubber can be identified chemically in collected debris (ref. 3). However, the debris contains only minor amounts of rubber contaminated by oil, exhaust fumes, and dirt from many sources. Since indoor tests seldom match road performance and since in many cases the abraded tire surface looks different from a normally worn tire surface (ref. 4), the debris from accelerated tests may not be representative of that generated at the road.

Cardina (ref. 5) has used the natural collection and concentration of debris by snowbanks along expressway routes to show that rubber debris can be found and identified. The concentration of rubber was low but unmistakable. Similarly, Pierson (ref. 6) collected airborne dust close to a heavily traveled industrial highway and chemically identified styrene-butadiene rubber (SBR), also at low concentrations.

In this work, we have tried (1) to collect debris worn off a single tire in normal road use, (2) to characterize the losses as to solids, vapors, or gases, (3) to find the effect of several known tire-wear parameters on the generation of debris, and (4) to determine the possible fate of that debris. In much of what follows, the term "tire dust" will mean "tire-wear debris."

Estimates

A typical new passenger tire (G78-14) weighs about 11.8 kg (26 lb). Tread wear down to markerbar safety limits removes about 3.5 kg (7 lb) of tread rubber in a normal road life of 40,000 kilometers. This is equivalent to an average loss about 90 mg/km over the life of the tire. This average wear rate compares to a loss rate (ref. 2) of about 24 mg/km at 120 km/h (75 mph) in cruise driving, increasing to about 490 mg/km in cornering at 48 km/h (30 mph) at a 2° slip angle. Direct measurements on the tires used in these experiments ranged from 60 to 120 g/1600 km, dependent upon both the tire itself and its position on the car.

Since we attempted direct pickup of tire dust in road service, we could expect sample sizes about 60 mg/km, even at the best. In actual practice, we collected far less than this. As shown later, we obtained what looked like reasonable aliquots, without ever approaching a material balance.

Tire losses amounting to 87 mg/km seem small in magnitude. However, if one uses the estimate of 90 million cars on the road in the United States (1970), each car driven about 22,500 km (14,000 miles)/yr, the total tread loss amounts to 0.72×10^9 kg/yr, (1.6×10^9 lb/yr).

This amount of tire dust was a major fraction of new rubber production in 1970, 1.6×10^9 kg. The tread loss estimated above includes carbon black and oil, so that the real rubber content is about 60 percent of that indicated. Even so, roughly one third of all the new rubber produced in this country is worn off tires.

EXPERIMENTAL

Qualitative Demonstrations

Road collection. Tire dust can be collected during real road service by mounting a sticky catchplate immediately downstream of a tire. One such installation is shown in figure 1, mounted on a front-drive car. Several factors prompted this initial attempt:

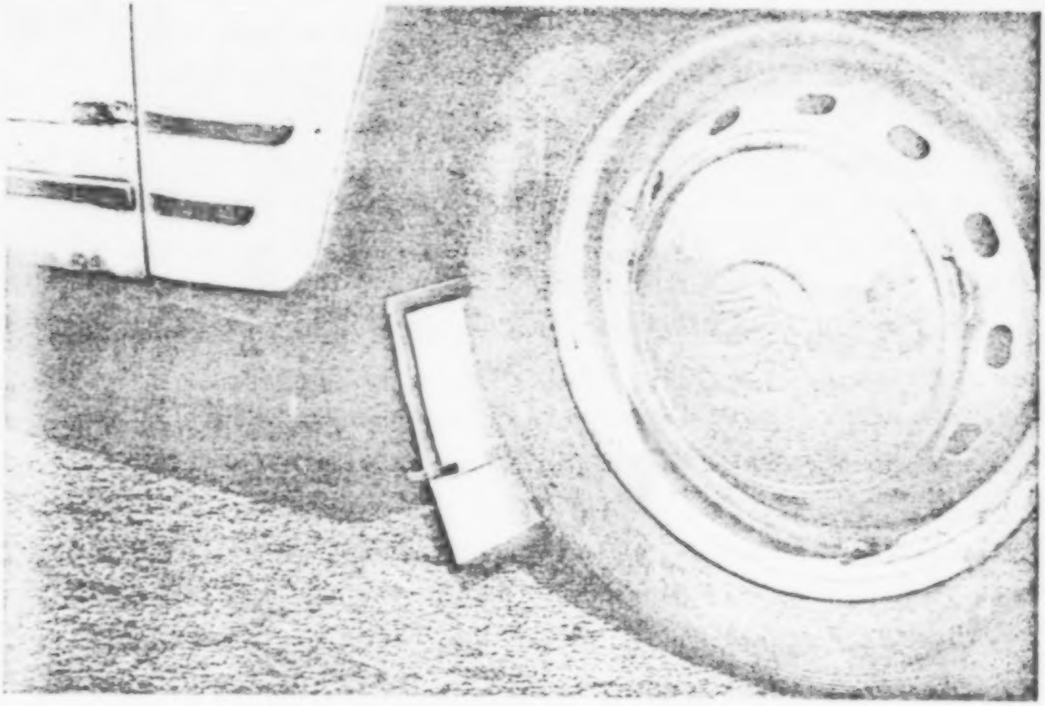

Figure 1. Wheel well and "sticky" catch plate.

(1) a conveniently located anchoring clamp was built into the car, (2) normal driving torque provided for wearing abrasion, and (3) availability.

Tire dust and associated road particles are generated during contact, then thrown back in a tangential pattern. The catch pad, covered with glycol-wetted paper, is located midstream, but its presence diverts the air stream and causes fractionation of particles. Large particles have sufficient inertia to impinge on the pad; small particles stay airborne as the wind sweeps across the surface and, hence, are not found in their expected proportions. The accumulation of debris on the catch pad was not uniform; rather, it was denser at the bottom. The bottom of the catch pad frequently disappeared during test runs, abraded off by simple erosion or lost abruptly during bumps.

Debris caught on the filter paper surface was examined under the microscope, both in situ and by transfer-mount techniques. The debris was also washed off the catch paper by a water spray, concentrated on a smaller filter pad, then analyzed chemically.

Identification. A photomicrograph of the debris caught this way is shown in figure 2. The black irregular chunks are rubber particles worn off the tread of the tire. Sand, silt, and other foreign matter are also visible. Contrast can be sharpened, paper eliminated, and some vertical concentration achieved by an Aroclor resin transfer technique, as shown in figure 3. Both photos are at 150× magnification.

Particle sizes range from 100 to about 5μm, the lower limit of resolution for this system. Shapes range from "sausage rolls" to rough spheres.

The irregular black particles are the tire-tread debris, identified as follows: (1) They look like rubber particles obtained from laboratory wear experiments. They are black, even at this small size, from the

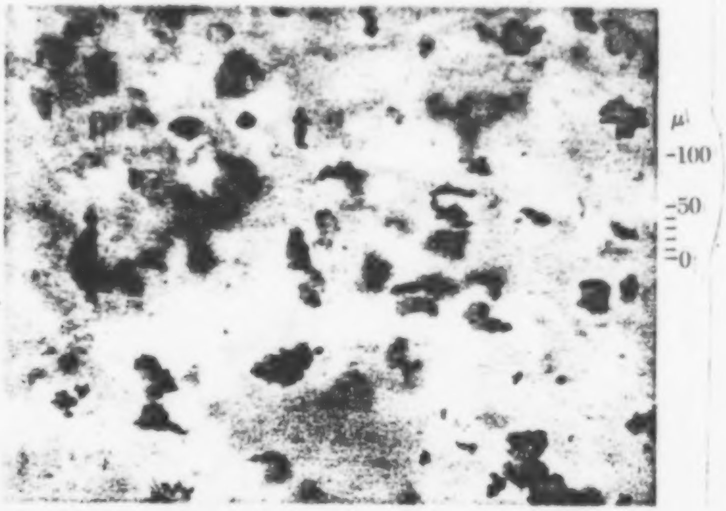

Figure 2. Tire and road debris caught on sticky plate. Black particles are rubber debris. Grit and cellulose are also distinguishable.

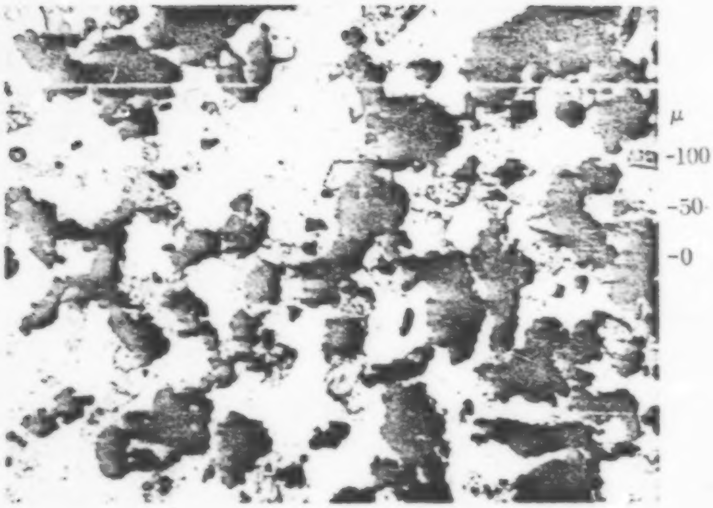

Figure 3. Tire debris transfered to Aroclor mount. Magnification 150×. Sand and concrete are obvious.

reinforcing carbon content. (2) Individual particles swell in chloroform, then deswell upon evaporation of the solvent. This proves that the particles are not a soluble black tar. Only a crosslinked material swells and deswells in this manner, i.e., rubber. (3) Individual particles float in chloroform, while siliceous debris sinks. The density of tread rubbers is about 1.18; chloroform, about 1.49, and silica-rich materials, over 2. (4) Infrared spectroscopic techniques affirm that SBR is in the collected tire debris. Agreement with a sample cut from the tire is excellent. This particular tread is an SBR compound without detectable amounts of either NR or CB blends. The absence of these latter rubbers in the collected rubber dust shows that tread dust from trucks or other modern cars is not a confusing contamination from those sources. (5) Ignition about 450°-500°C leaves a residue ranging from 50 to 80 percent. This agrees well with a visual estimation of the amount of sandy grains, which have a density about twice that of the rubber.

Particle analysis. Particle size distribution of tire debris affects subsequent reactions and disposal. Fine particles can remain airborne, while coarse particles settle out, along with other kinds of dust and dirt. Fine particles, with a high specific surface area, would be expected to oxidize rapidly, while coarse particles would oxidize more slowly.

While this tire debris collection technique is subject to experimental criticisms and improvements, this sample was collected in real service on the road from a moving car. Hence, despite limitations these samples were measured, and particle sizes were counted to get a distribution microscopically.

The volume in apparent mm^3 was computed for each particle. Particle size counts were made and summarized in logarithmic cell-size ranges, each double its predecessor. At 150× magnification, 1 mm^3 apparent volume is 295 mm^3 real volume. Since the particles are sausage shaped, an "equivalent diameter" is defined as the diameter of a sphere having the same volume.

Particle size distributions for three runs are presented in figure 4, on log volume, cumulative probability coordinates. Partial identification is listed in table 1.

Several tentative conclusions can be drawn from this qualitative presentation. (1) Tire dust in the size range 5 to 100μm equivalent diameter can be found in actual road wear experiments. The geometric mean particle is about 25μm equivalent diameter. (2) Collection efficiency is low. The quantities caught were about 1.9 mg/km,

Table 1. Identification of runs in qualitative demonstration

Run	Road	Distance, miles	Speed, mph	Particle count	Amount collected, mg	Rubber content, mg	Wear catch, mg/mile
634B	I-271 NE	3.9	60	51	49	12	3
634C	I-77 S	5.8	60	75	92	23	4
634D	I-77 N	5.4	44	97	77	19	3.5

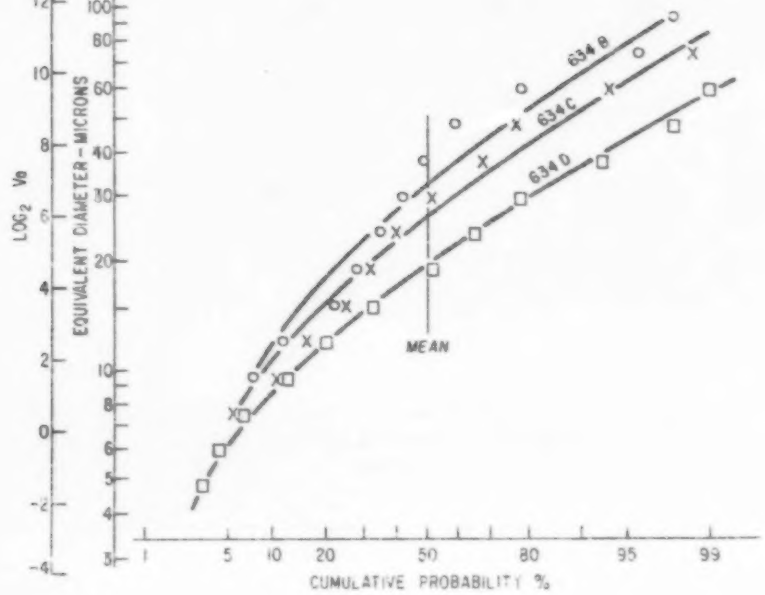

Figure 4. Particle-size distribution of tread debris from sticky plates.

compared to a computed average wear rate about 31 mg/km on this small car. In addition, the collection plate system tends not to collect the finer particles. (3) Particles below 10μm equivalent diameter are relatively sparse. Particles below 3μm were not detected. (4) Improved technique of collection and improved particle size counts are required in order to define the distributions better and the way they vary with speed and load.

Quantitative Experiments

An improvement tried next involved a vacuum filter system in which air was drawn through a glass fiber filter to capture the particle.

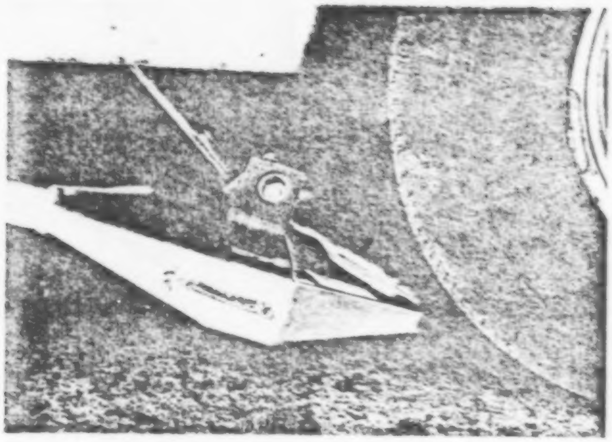

Figure 5. Close-up of modified filter system. Centerline pickup 2 in off road. Vacuum cleaner mounted in trunk is not visible here.

Revised techniques. It was ultimately realized that air entered the front orifice of the collection duct at a ram-velocity faster than the vacuum pump could pull it through the filter. Excess air circulated around, then spilled out the sides, carrying with it part of the road debris. While the portion caught on the filter may be a true aliquot, such an assumption could not be proven. Roughly only 1/20 of the air that enters the front can be pumped through the filter.

Use of a small orifice about 2 × 4.5 cm was a simple way to achieve isokinetic sampling. The modified pickup and filter system is shown in figure 5. This is a rear-wheel installation on a conventional sedan.

Road runs were continued on Interstate 77 near Brecksville, Ohio. The restricting orifice resulted in smooth uniform distributions of debris over the filter, but lowered the amount encountered and retained. Hence, only the particle size measurements were made. Transfer slides were made, photographs taken, and particles counted. Distributions are plotted as figure 6.

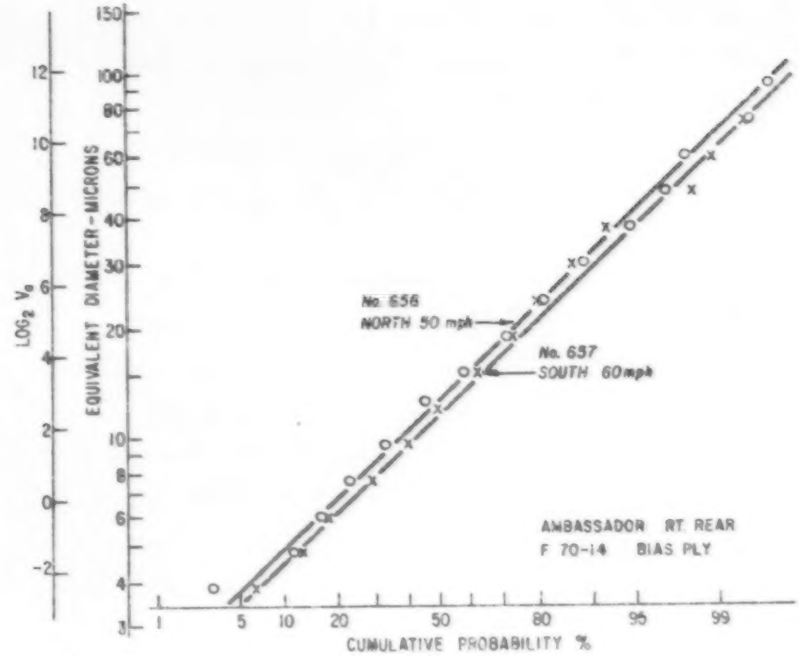

Figure 6. Particle-size distribution of tire rubber debris, "isokinetic."

Note that the eccentricity or sausage shape of the particles does not enter into this discussion. While many of the rubber particles are three to four times as long as wide, this information has not been used as yet.

The particle size distributions shown in figure 6 are linear within reasonable estimates of experimental error. This means that the log size distribution is Gaussian. This happens also to be a common or widely encountered distribution for chip sizes in grinding and crushing operations. The analogy may be coincidence, but does offer some confidence in experimental procedures. This distribution has been reported for airborne particulates collected in "dirty air" exposures, although much smaller particles are involved (ref. 7).

The use of the log scale on the ordinate axis modifies some of the statistical treatments normally derived from the use of the probability-paper scale (ref. 8).

The midpoint or "half-life" value defines a geometric mean analogous to the simple arithmetic average. Similarly, the geometric dispersion replaces the standard deviation σ.

The geometric mean particle has an equivalent diameter about 12 μm. Particles ranging from half that diameter to twice that, i.e., from 1/9 to 9× that volume, are within one dispersion unit, or total about 2/3 of all the particles encountered. Particles having more than -2g' dispersion, i.e., having equivalent diameters less than 3 μm, are statistically rare, less than 1 percent. In a physical sense, this implies that their concentration is so low as not to be important.

While separate lines, i.e., curve-fitting operations, were drawn for runs 656 and 657, the dispersion of the data does not justify it. The same particle size distribution, within experimental error, is obtained at nominal 80 (50 mph) and 97 km/h (60 mph) cruising speeds. The amount eroded off at the higher speed is larger, but the particle size distribution is the same. As shown later, a wider range of speeds (77-105 km/h), is needed to show a significant change in the size distribution.

This discussion on distribution needs additional emphasis. The distribution curves are based on number fraction. The larger sizes account for most of the weight lost from the tire. A single large particle weighs more than a small particle by the ratio of cube of the equivalent diameter. A particle having a dispersion +g, or 2.1× the mean, 12 μm, has a volume nine times the mean. Similarly, the small particle at -g or $(2.1)^{-1}$ × the mean has a volume

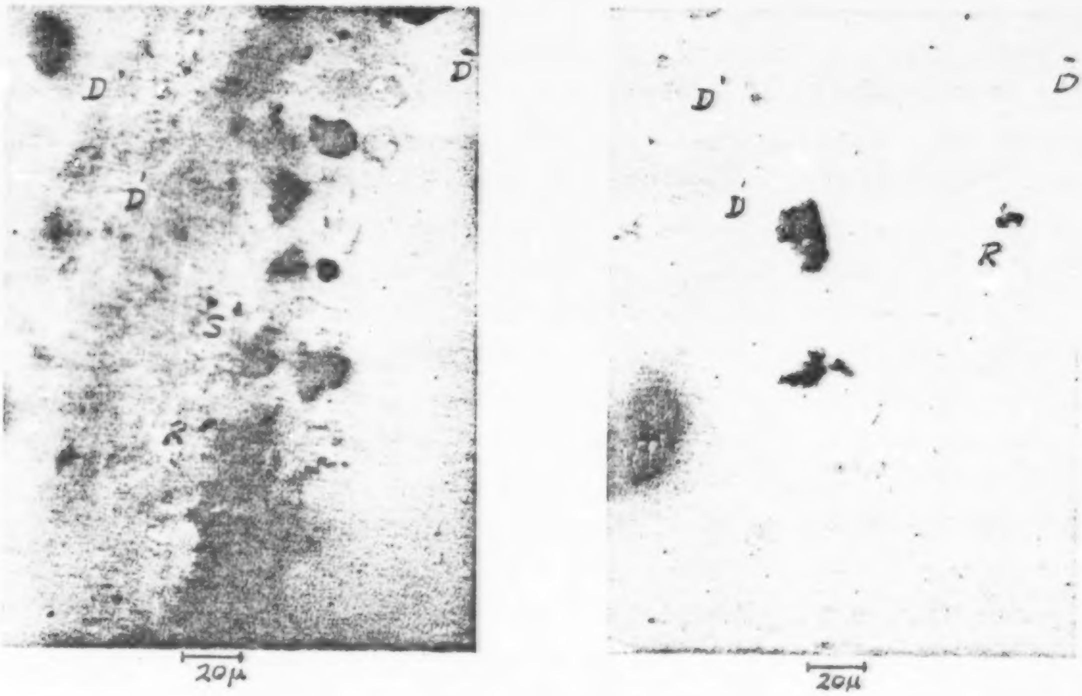

Figure 7. Tire debris photo micrographs @ 350×. Particles labeled D are dirt on the lens. Particles labeled S are road silt or silica. Particles R may be rubber. No small black particles less than 2μm diameter can be identified.

roughly 1/9 the mean. These large and small particles then compare about 81 to 1, both volume and weight. In the opposite sense, a few small particles have negligible weight.

Micron size particles. Thompson (ref. 3) implies that small airborne rubber particles might be small enough to escape nasal filtering and hence could enter the lung structure. He states that particles above about 5μm are efficiently filtered in the nasal passages and should not cause any health problems.

Therefore, the importance attached to rubber particles having an effective diameter less than 3μm has required more than a statistical search for their presence or absence on the microscope slide. In one particular experiment, slides, used in the counts of run 657, were reexamined both at high dry magnification and in oil immersion to look for particles too small to be easily visible at the 150× magnification, which was used routinely. In figure 7, two photomicrographs are presented showing many artifacts, which could be eliminated by various tests to leave on each slide one particle which might be rubber. Even so, these are within the range expected or extrapolated from the counts at larger sizes. If small particles of tire rubber do exist, this technique does not catch and identify them.

For improved technique and a better experiment, a Millipore filter was installed in the vacuum line to sample part of the air stream. The regular glasscloth filter described earlier was used as the roughing filter, backed up by a Millipore filter with a nominal port size 0.45μm diameter. The residue on the Millipore filter was examined directly in order to avoid problems of losses in transfer. Particles from the glass-cloth filter are shown in figure 8 at low magnification, emphasizing the sausage-shaped particles. Figure 9 shows the rough surface of the larger particle at higher magnification, showing also that road silt is imbedded in or associated with the rubber.

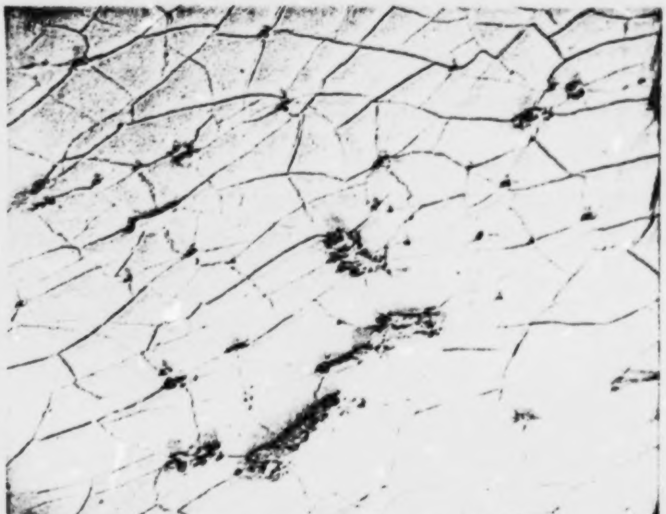

Figure 8. S.E.M. @ 50× on initial filter.

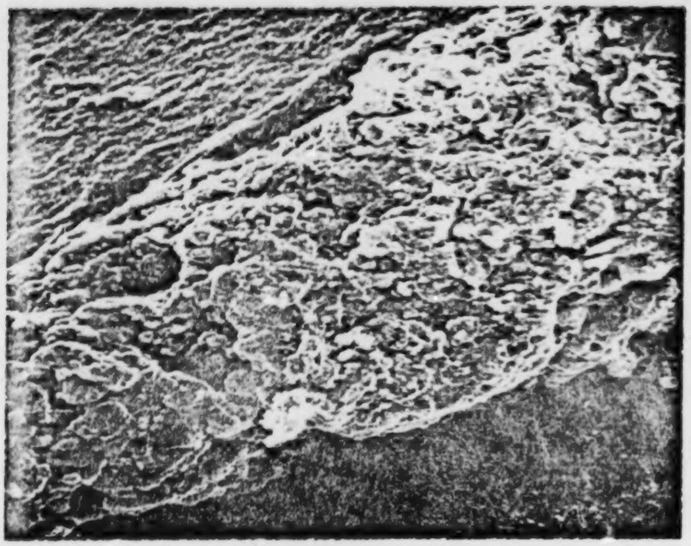

Figure 9. S.E.M. @ 1000×, detail of large grain of figure 8.

A particle caught on the Millipore filter is shown in figure 10. This has a read size about $3 \times 2 \times 2$ μm^3. This was an isolated particle and the smallest one found, but fairly typical in other respects. The surface does not closely resemble that of the "rubber sausage"; whether this is a tire-dust particle is not certain. However, very few particles of this size or smaller can be found. Hence, the concentration of small rubber particles, 3μm and below, is below present limits of detection.

Effect of road variables. A wide range and variety of road and tire variables affect the wear of tires and, presumably, the particle size distribution. These experiments have been run under conditions to minimize changes and were accordingly confined to a short stretch of interstate concrete highway in order to standardize that condition. Road surface affects tire wear rate (ref. 2) and would be expected also to affect particle size distribution. It does.

Experimental investigation of this suspected effect was tried in a set of three runs, labeled 672A, B,and C. The data are presented in figure 11.

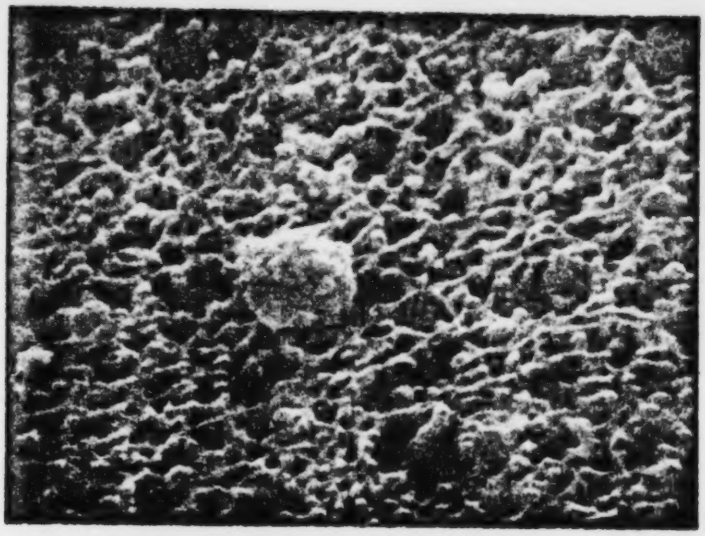

Figure 10. S.E.M. @ 5000×. This is a single grain on 0.5m diam. millipore filer.

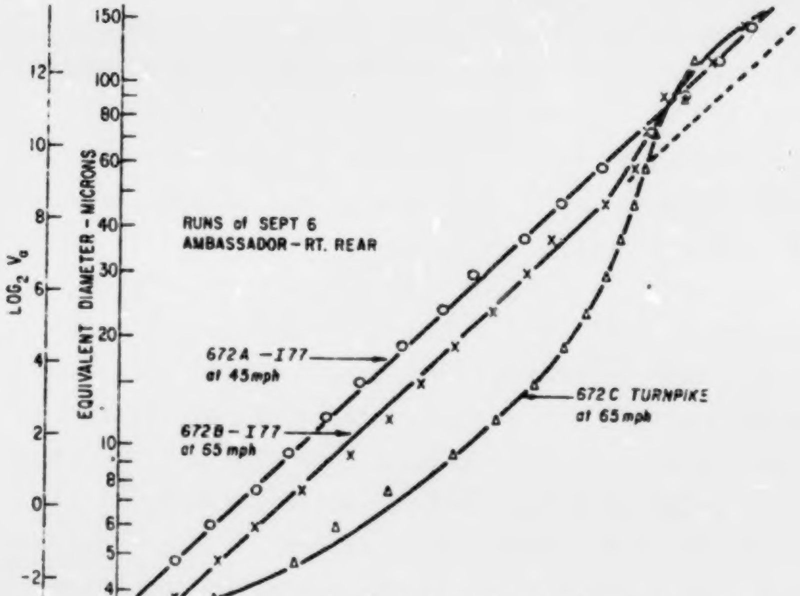

Figure 11. Particle-size distribution of tire rubber debris.

The curves of runs 672A and 672B, on concrete, are linear and have the same slope or dispersion as run 656 of figure 8. The deviation from linearity of 672B at the upper end of the scale is due to a few large particles which may be agglomerates. The mean values of runs 672A and 672B differ slightly from the mean of run 656, figure 7, as shown in table 2.

Since runs 672A, B, and C involve a different tire than the runs 656 and 657, several variables have been changed. However, note that the dispersion g on concrete is remarkably constant in these four runs.

The relationship for run 672C on asphalt, shown in figure 11, suggests a different collection and/or wear mechanism. Not only was the distribution different, but the amount collected was less than on concrete.

Note that the particle size curves in figure 11, run 672C, show an abnormal amount of the large particle sizes. This is not a bimodal distribution, but it is a skewed curve distinctly different from the log-normal distributions obtained from concrete. The amount and size distribution of tire dust that is collected from an asphalt road is different from tire dust collected on a concrete road. This situation requires further investigation.

Table 2. Statistical constants from particle size experiments.

Run	Speed, mph	Mean apparent volume			Mean equivalent diam. x50, μm
		Z50	V50	g	
656	50	2.7	6.50	9.20	12.4
657	60	2.4	5.27	9.20	11.6
672A	45	5.2	37	9.4	22.3
672B	65	4.0	16	9.2	16.8
672C	65	1.0	2.1	6.6	8.4 (Asphalt)

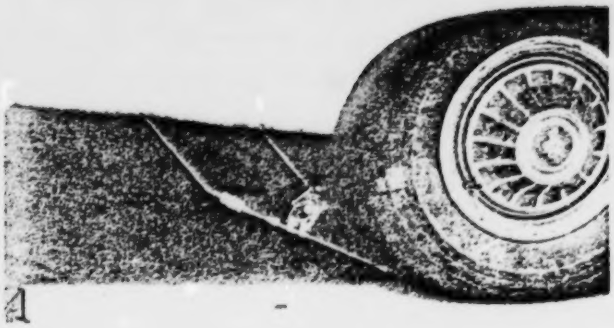

Figure 12. View of emmisions probe at right rear wheel of car.

Partial summary. Tire dust is generated in larger amounts at higher speeds, but the mean particle size is smaller. The effect of asphalt as a road surface changes both amount and distribution of tire dust particles.

Gaseous emmissions. Tires, in normal wear, abrade against the road surface to generate dust and debris that can be caught on a filter and measured. Tires may also evolve gases and vapors either by direct emission or from oxidation mechanisms. An attempt was made to find such, without success. This negative result is important.

Tread rubber is a hydrocarbon compound subject to oxidation, low-temperature pyrolysis, volatile emission of low molecular weight fragments, and other related emission mechanisms. With appropriate sampling and modern sensitive instrumentation, hydrocarbon emissions in the range of parts per million in the surrounding air should be detected. While hydrocarbon concentrations in the atmosphere near a car are easily detected and measured, incremental gains above this level in the region of the tire are too small to be measured.

One experimental arrangement is partly shown in figure 12 and diagrammed in figure 13. A portable gas chromatograph with a flame-ionization detector was carried in the car. Gas samples were pulled from just behind the contact area of the tire and from several nearby comparison locations. Engine exhaust was also sampled.

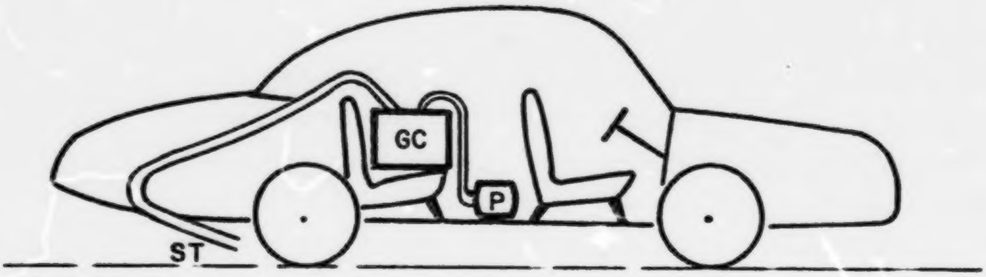

Figure 13. Schematic of Volatile Emissions experiment. ST, Stainless steel tubing pickup downstream from tire. GC portable gas chromatograph. P, positive displacement pump.

In one run, chromatographic separation was attempted, unsuccessfully, using a packed column. In later runs column fractionation was eliminated to gain greater input sensitivity. Instrumental or background response to gases pulled from the air either ahead of or behind the tire gave a signal equivalent to 3 to 5 ppm of hydrocarbon, depending upon local conditions, i.e., moving or stopped car, engine running or dead, direction of breeze. In no case was there an obvious difference before or after tire contact. Exhaust emissions were large, on the order 50 to 150 ppm, and changed as expected with warmup, idle, and cruise conditions.

In summary, since every other check showed that the equipment was operating properly, the results should be believed. Gaseous hydrocarbon emission from normal tire usage is too low to be measured.

Since no measurable hydrocarbon emissions could be detected, and since oxygen is absorbed within the structure of the rubber (ref. 9), not evolved as CO^2 or H^2O until very late stages of oxidative breakdown, particulate erosion of the tire tread is the only important loss mechanism.

RESULTS AND DISCUSSION

Dispersion, Degradation, and Disposal

Dispersion. Tires wear out, generating tire dust. This seems to be the dominant mechanism, since volatile hydrocarbon emission cannot be detected. Since total tread loss is estimated about 5×10^8 kg/yr into particles with mean effective diameter about 20 μm, one would expect to find tire dust everywhere. However, experience shows that this is not so.

If the tire dust were spread uniformly over the 6×10^6 km of highway in the continental United States (in 1970) (ref. 10), average width about 7.5 m, the concentration of rubber would be about 1.6×10^{-3} kg/m/yr. Such amounts are not seen except in skid marks, which disapear within weeks or months.

A tire-dust particle with an 18 μm diameter will have a Stokes Law settling velocity about 1 cm/sec. This size particle is fairly close to the mean equivalent diameter listed in table 2. Particles near this size are easily aerodispersed by air currents around moving cars.

Tire-dust particles should be airborne, but settle out slowly down wind. Rubber concentrations should be identified both airborne and on the ground, as shown by Pierson (ref. 6) and Cardina (ref. 5). Dirt samples from the berm of Cleveland Massillon road in Brecksville showed detectable SBR content by infrared techniques. A portion of the spectrogram is reproduced in figure 14. The peaks are not large, but easily recognizable. Comparisons on soils a hundred meters from the road showed no infrared absorption relatable to rubbers.

Degradation. Oxidation of rubbers by chemical and/or physical mechanisms is well known to rubber technologists. Oxidations of rubber

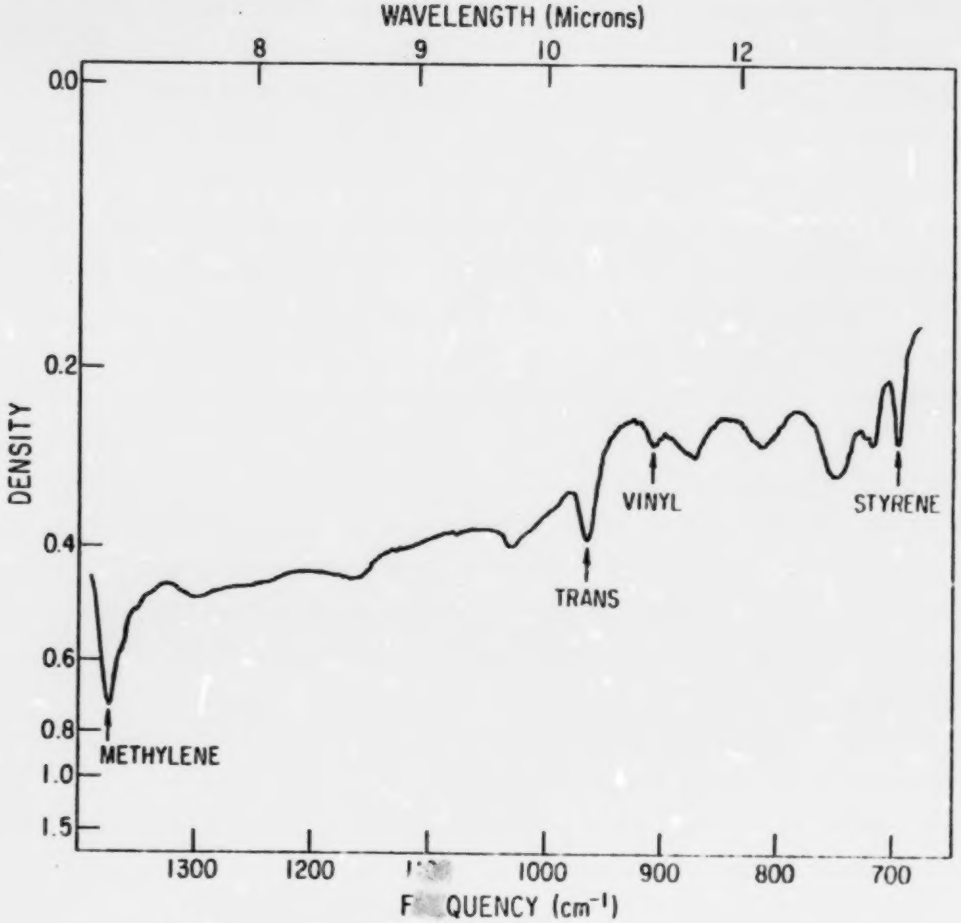

Figure 14. Infrared identification of SBR residues in roadside dirt.

should be discussed in several categories called (1) initial, (2) intermediate, (3) extensive, and (4) complete oxidation. Initial oxidation (1) is related to the addition of oxygen to the dienic structure, without appreciable evolution of CO^2 and with distinct changes in physical properties (ref. 11). Intermediate oxidation (2) involves the evolution of some CO^2 and H^2O, with extensive physical degradation of the rubber but without significant evolution of volatile fragments in the C^4 to C^{10} range. Extensive oxidation (3) results in well-defined fragments split out of NR rubber, such as methanol, acetaldehyde, and levulinaldehyde in stoichiometric ratios to CO^2. Extensive oxidation of SBR gives a wider range of products ranging from CO^2, formic acid, acetone, acetaldehyde to a group of 3- and 4-carbon oxidized hydrocarbons (ref. 12). Complete oxidation (4) is combustion and results in metal oxide and sulfate residues, and CO^2 and H^2O.

Initial oxidation of tread dust by direct chemical and/or photo-induced oxidation mechanisms is relatively slow because of the low temperatures in soil, 15° to 30°C. Compare this to temperatures measured in the tire, 50° to 125°C and above, depending upon location in the tire and severity of service. The lowered temperature range more than compensates for the high surface area of the tire dust. Antioxidants used in the tire are still found in the tire dust, affording some protection to the rubber. Even so, oxidation-rate measurements on ground tire tread were attempted in this laboratory with an improved oxygen absorption apparatus (ref. 13).

No detectable oxidation could be measured at room temperature after 168 h or at 40°C after 264 h. At 100°C, "Normal but slow" oxidation rates could be measured. This can be expressed as roughly a 5-year period for half the rubber to be oxidized. A half-life of 5 years at 100°C means much longer life at ordinary temperatures if simple oxidation is the only degradation mechanism.

Ozone attack on rubber is more severe than simple oxidation. However, ozonolysis of the rubber in the soil is not expected because cellulosic materials and residues are so reactive toward ozone that no ozone would reach the rubber dust.

Hence, the elimination of tread dust in the soil by ordinary chemical and/or physical oxidation is slow reaction. This statement is supported by extensive experience with rubber jackets on buried cables and other underground usage where deterioration and damage is traced to rodents, insects, and fungi (ref. 14). Oxidation is not important in comparison to greater damage caused in these other ways.

If chemical oxidation is not important as a mechanism for eliminating tire dust, one should consider biooxidation, biodegradation, and biological utilization. Biodeterioration, biodegradation, and metabolic transformation are progressively more severe steps in the biological decomposition of organic materials. In this discussion, biodeterioration is the loss of any measurable physical property without appreciable loss of mass or change of form. Biodegradation is related to a major change in chemical structure, a decrease of molecular weight, and extensive change in physical properties or in form. Metabolic utilization is the use of part of the carbonaceous content as oxidation to CO^2 and simultaneous synthesis of hydrocarbon residues into growing cells.

Depending upon circumstances of exposure and upon the microflora encountered, rubber compounds cover all extremes from ready susceptibility to extreme resistance. Heap and Morrell (ref. 15) have pointed out the confused and sometimes contradictory evidence presented in the literature. Various authors not only use different techniques of evaluation, but establish different criteria of failure. Hence, in this investigation it was considered sufficient to show that SBR compounds can be biodegraded under lab conditions. Rigorous proof that SBR compounds are extensively biodegraded in soil conditions, i.e., in natural exposure, has not been attempted.

A major factor contributing to confusion in experiments and reports on the biodegradation of rubbers is the biocidal activity of mercaptobenzothiazole, TMTD, and related compounds (ref. 16). Accelerator residues inhibit biodegradation until they have been depleted below critical limits by aqueous leaching or other chemical reactions. Thus, the same initial compound could be described as nondegradable by short time tests, and extensively degraded in longer exposure or in more severe environments.

Natural rubber latex, smoked sheet, and vulcanized compounds are readily attacked by a variety of bacteria and fungi (ref. 15, 17-19). One variety of streptomycetes has specifically adapted to rubber latex, readily consuming it as its sole source of carbon (ref. 20).

SBR and its compounds are slowly attacked by many of the bacteria and fungi that degrade NR compounds. Recently, Nickerson (ref. 21) identified several fungi grown on OESBR compounds and also described extensive biooxidation of the rubber crumb.

Several laboratory experiments on biodegradation of tread rubber have been attempted. A variety of molds not fully identified were grown on shavings obtained from tire-trueing machines in current production. Growth of molds was obvious after about 10 days.

A wide variety of molds can be grown on rubber chips and particles, given appropriate conditions. Mold growth on the rubber is obvious; mold growth at the expense of the rubber was not demonstrated conclusively. Extender oils, antioxidant waxes, stearates, and/or other ingredients could provide nutrition either preceding or accompanying degradation of the rubber. Cometabolic utilization is a common occurrence, i.e., a fungus or bacteria uses one chemical as a food or energy source, but secretes enzymes that attack or degrade other nearby materials. In turn, another species of fungus uses those "predigested" products in its own growth cycle, often making byproducts useful to the first fungus. Hence, fungal growth of any kind is evidence of bioattack, probably on the rubber, but not proven by this simple demonstration.

A different experiment was tried in order to look for chemical evidence of biodegradation. Perfusion reactors, as shown in figure 15, were set up with different rubbers and innoculates. A perfusion reaction is a perculating diffusing system. The mineral content and available carbonaceous material, i.e., the rubber, make up a nutrition system that favors the growth of particular bacteria. These bacteria concentrate in the system, growing faster than other competitive species.

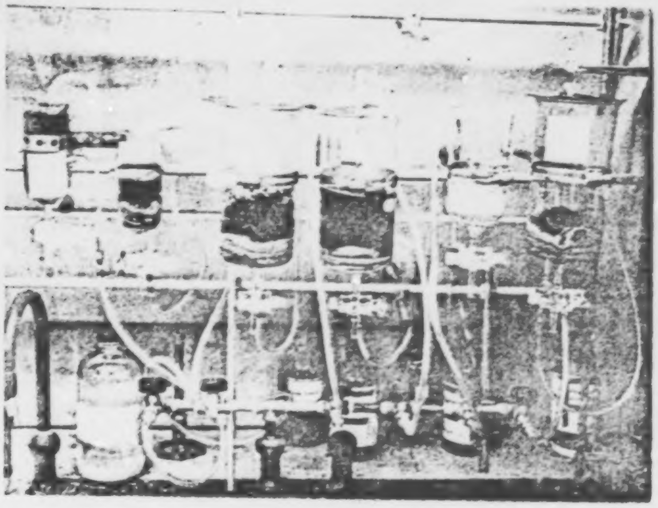

Figure 15. A battery of perfusion reactors, 300 and 1000 ml sizes.

Microscopical examination of the aqueous fluid showed a wide variety of bacteria active and mobile. Photography of the live cultures has been attempted without success. Photomicrographs of stained, fixed bacteria were obtained to show that bacteria can grow in the presence of rubbers.

Degradation of the rubbers aged in the perfusion reactors can be shown by chemical analysis of the residues after exposure of 30 or 60 days. Reactor experiment No. 4 was charged with a natural rubber tread stock, ground to about 100-mesh sieve size. Changes in the infrared curves in the 6μm region related to oxidized structure of rubber are shown in figure 16. The original curve shows only a trace of structures related to --C--O in acid, aldehyde, and ketone structures. After bioexposure in the perfusion reactor at 30 and 60 days, greatly increased adsorption in this region is evident, together with a smearing of the infrared peaks. This loss of detail is ascribed to a range of partly oxidized local structures differing in neighboring side groups. First, this gain in oxidative structure is much larger than expected from simple chemical oxidation at room temperature under these exposure conditions. Quantitative extimates of this large gain cannot be made

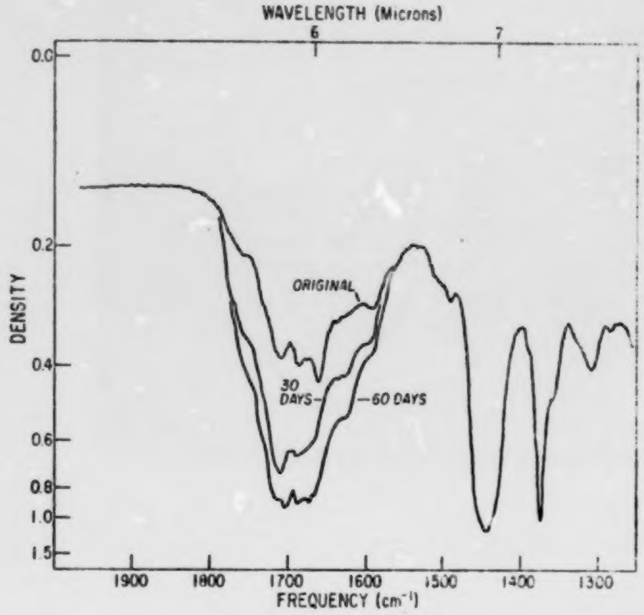

Figure 16. Infrared spectra showing changes in oxidized structures in an NR tread compound during perfusion exposure.

because of many complicating and poorly controlled factors. Second, laboratory records kept during the preparation of these spectra showed that the solubility of the rubber had been altered. The samples aged 30 to 60 days were very soluble in o-dichlorobenzene and did not precipitate normally when diluted with methanol. This proves a decrease in molecular weight, along with a change in chemical structure.

Biochemical oxidation and degradation have been demonstrated in the laboratory only.

Similarly, reactor No. 5 was charged with an OESBR/CB tread compound, obtained from a knife-type trueing machine. Changes in infrared structure indicative of oxidation are shown in figure 17. These are similar to but smaller than those shown in figure 16 for the NR compound. The same biooxidation occurs; the rate is lower. The same increase in solubility was also noted, but this too was smaller than in the NR comparison. This demonstrates biooxidation without distinction between bacterial and fungal agents.

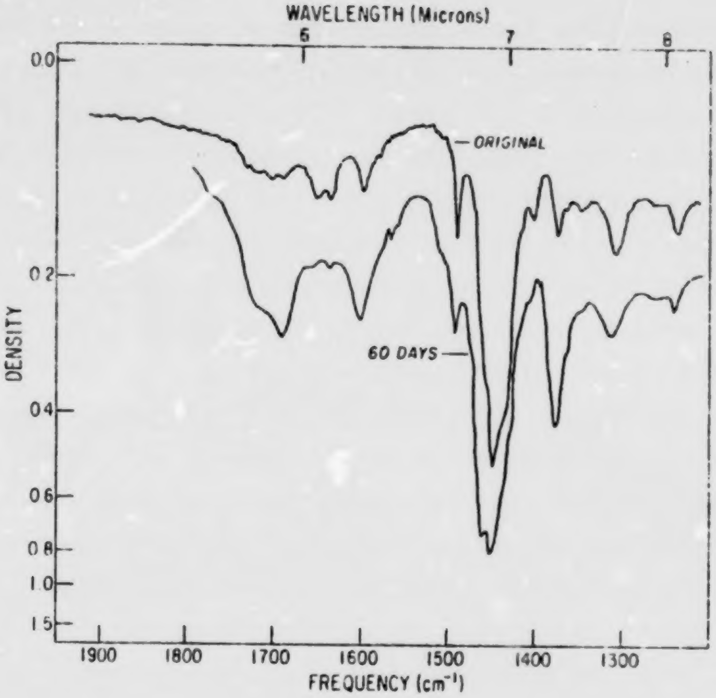

Figure 17. Infrared spectra showing changes in oxidized structures in OESBR/CB tread compound.

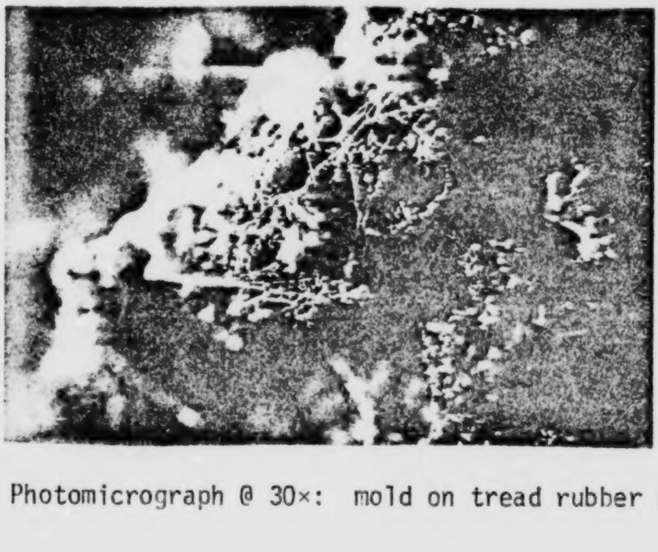

Figure 18. Photomicrograph @ 30×: mold on tread rubber grindings.

In a later experiment, the difference between bacterial growth and fungal growth was inadvertently demonstrated. Reactor 697, charged with grindings from the OESBR/CB tread compound showed little evidence of bacterial growth in the circulating liquid in 30 days perfusion aging. Analysis via infrared techniques showed very little oxidized structure at that time. The reactor contents were emptied into a jar, which was set aside while other experiments were run. After 2 weeks' rest or incubation at room temperature, the contents of the jar were covered with mold. Direct growth on the tread rubber grains is evident in the photomicrograph of figure 18. Sectioning, staining, and further microscopical inspection were tried in order to show penetration of the tread granule by mycelium of the fungi. Evidence of such penetration was obscured by the carbon black content and cannot be reported conclusively. However, since mycelial penetration into transparent polyester urethanes has been observed; similar behavior is suspected here. Note that fungal growth did not occur in the circulating perfusion reactor. Extensive growth did occur when the moist rubber was left undisturbed.

Previous sections have presented evidence that rubbers are subject to biooxidation. The extender oils in rubbers are also susceptible, probably more so than the rubber itself. The direct utilization of carbon black has also been known for some time. "In 1908 Porter observed that aerobic soil bacteria, especially a coccus, which was obtained in pure culture, slowly oxidized amorphous carbon in the form of charcoal, lampblack, coke and peat...." (ref. 22).

Recapitulation. Tire dust generated at the road is dispersed by air currents around the car and settles out on the surrounding landscape. These particles oxidize very slowly in simple, well-known oxidative reactions. However, in the soil they can be biooxidized, degraded, and decomposed by a wide variety of bacteria and fungi. Under appropriate conditions in moist soil, the rubber dust is extensively degraded and altered within months. Under unfavorable conditions for decay, residues (and relics) can be preserved for decades (ref. 23).

Material Balance

The experiments in which tire dust was caught were all experiments of low yield. The amounts recovered were on the order of 2 to 3 mg/km. The low collection efficiency is easily rationalized. The geometry of the pickup aperture is sketched in figure 19, suggesting that only a fraction (4.5 percent) of the "dusty area" is sampled. A correction for this low efficiency gives an indicated loss about 45 mg/km.

A distinct improvement would entail a read road run with a complete material balance. Considerable time and effort have been spent trying to design such an experiment, but without success.

Innocuous Dust

While the particle-size distributions vary with speed and road conditions, only very few particles below 3μm effective diameter were found. Additional search effort to identify these particles was unsuccessful. Airborne particles 5mm and above are efficiently filtered out of human respiratory systems in the nasal passages. Particles about 2μm escape nasal filtering, could enter the lungs, and be retained by alveolar deposition according to Thompson (ref. 3). However, particles of this size were not found and seemingly are not generated.

SUMMARY

Tires wear out in normal use. Tread rubber losses have been investigated in order to find out if the rubber abrades to particles, degrades to an intermediate state, or oxidizes to volatile vapors and gases. Particulate erosion seems to be the dominant mechanism.

Particles worn from tires were first collected on sticky panels

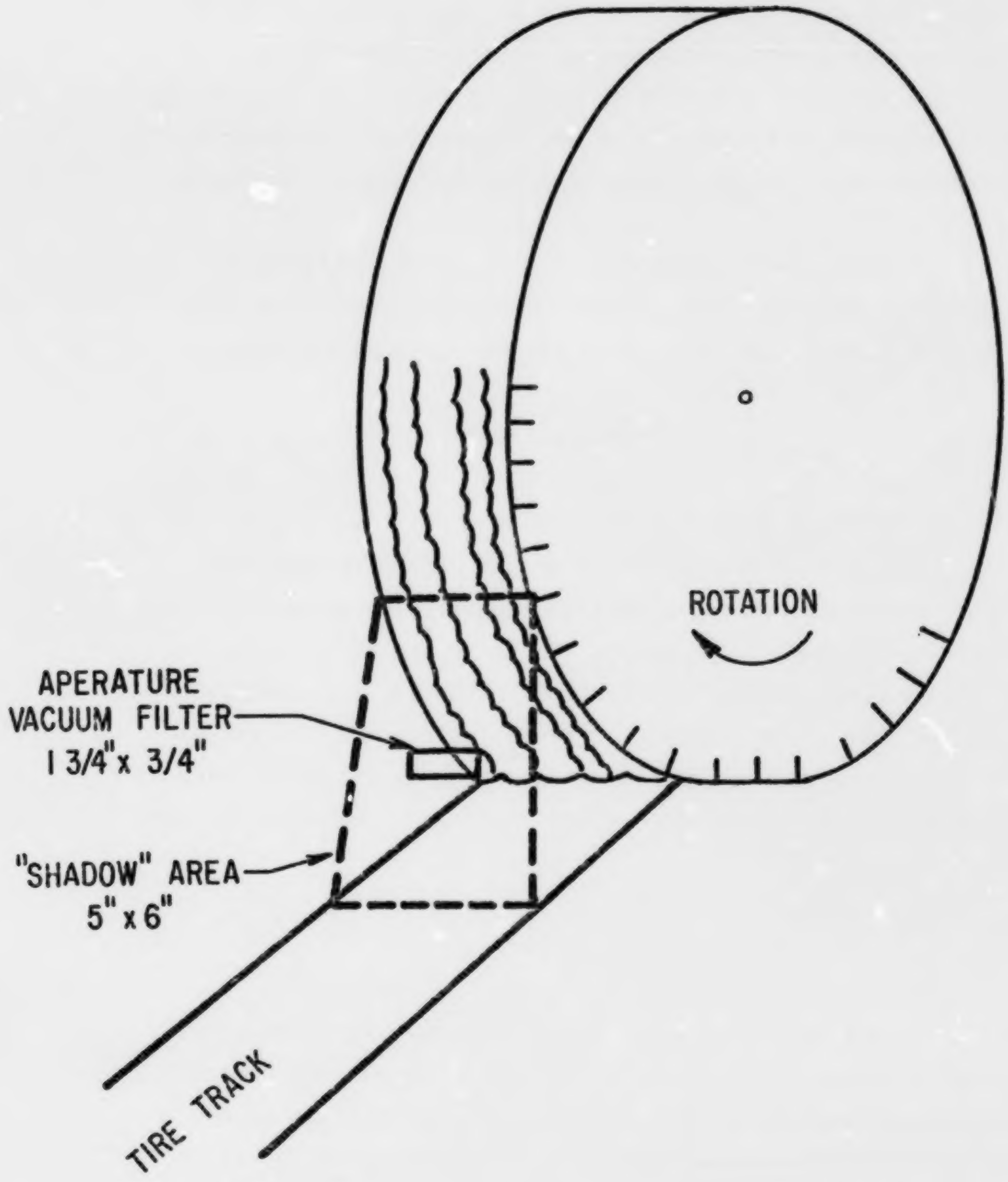
ROTATION
APERATURE
VACUUM FILTER
1 3/4" x 3/4"
"SHADOW" AREA
5" x 6"
TIRE TRACK

Figure 19. Schematic showing aperture for tire dust sampling compared to visual "shadow" of the source.

mounted under the car. The particles are not spherical but approach cylinders or sausage shapes as a limit. The particles range from about 0.1 mm equivalent diameter to a few microns minimum, in accord with the Schallamach description of tire abrasion.

Later an isokinetic filter system was developed. The particles caught on filter plates were examined, transferred to microscope slides, photographed, then counted to obtain particle-size distributions. Smooth distributions were obtained, linear on logarithm of volume, cumulative probability graphs. The geometric mean particle size is about 20μ equivalent diameter. The curve is sharply peaked on its log scale.

Special effort was devoted to a search for very small particles, from about 1/2 to 3 μm equivalent diameter. This is the diminishing tail on the distribution curve. Very few of these particles could be found.

Attempts were made to identify volatile emissions from a running tire, using chromatographic techniques and a flame ionization detector, without success. Since hydrocarbon loss as a vapor from tires is nil, particulate erosion is the dominant loss mechanism.

Tire dust particles have a high specific surface and are subject to oxidation. Simple chemical oxidation is slow, but biochemical oxidation at the soil under the combined influence of oxygen, photoexcitation, and enzyme catalysis can be rapid, returning the carbon content to the normal biological carbon cycle.

ACKNOWLEDGMENTS

This paper is a contribution from the Research Laboratory of the B. F. Goodrich Company. Contributions of several of my coworkers are acknowledged as follows: A. Veith on tire wear; P. Zakriski for chromatographic analysis; H. Diem for infrared analysis; J. Gianelos for X-ray tracer analysis; R. Smith for scanning electron microscopy; and P. R. Petroff for miscellaneous, extensive, mechanical help.

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DISCUSSION

Following papers presented by Dr. Pierson and Mr. Dannis

DR. PIERSON: I guess the main comment I want to make concerns Mark Dannis' allusion to the size, when he said that there is nothing smaller than 3 microns by mass. The work that we did, as I mentioned already, shows that in a severe situation most of the particles are indeed larger. In a mild-wear situation we had 60 percent of airborne rubber by mass less than 1.1 micron, and I point out that the mild-wear situation I am talking about is very similar to the mild-wear situation Mark was talking about. He mentioned a 45- to 65-mile-an-hour cruise. I did want to state the disagreement on this point, though I am not saying what the answer is. Other than that, it looks as if we prepared the same ground and are in pretty good agreement. I was glad to see that somebody was looking into the question. Once you have asked the question, "Where does the rubber go?" - the answer is, "Most rubber ends up in the soil." Then the next question is "What happens to that?" And I wouldn't get into that question at all. He did, and I think that at the present time it is the important thing to do.

[See supplementary comments by Dr. Pierson following the present discussion.]

DR. PIERSON: I had a couple of questions, Mark. Does anybody know yet what happens to the bacteriological degradation products themselves? Second, have you actually measured what was worn off the tires? Maybe you can conjure up a way to get a collection efficiency; that would be a nice way to tie the whole thing down. I wonder if you tried to do that?

MR. DANNIS: I'll try to answer the second question first. Yes, I did make the collection efficiency. We got a couple of friends and I drove the car 55 miles an hour for 700 miles to get the wear loss on each wheel. It is necessary to drive that distance because under loaded conditions and steady cruise the wear loss is only 30 grams per thousand miles. This is the direct weight measured on the whole tire--30 mg--3 grams per 1,000 miles is 30 mg a mile. Our average collection of rubber is between 4 and 5 milligrams per mile in pickup exposure.

Efficiency then is on the order of 7 to 10 percent and the aperture that I used, based on some type of pickup area where most of the rubber can be found, is at that same order of magnitude. I first only believed it was well above 90 percent of the total wear of the tire coming off as particulates. The number may be as high as 99 percent, but I am going to be conservative and say well above 90 percent.

Regarding the first question, "What happens to the material in the soil?" - I have been very impressed as a newcomer in soil microbiology. If you can get right on the action in the laboratory, you can prove it in the soil. I believe the rubber is first partly degraded to a humus or to a humic acid that has very beneficial effects.

There are some publications that appear in agronomy journals and show that the use of ground rubber improves the tilth in cultivation of dense clays, if it permits passage of water, and improves the texture of sandy soil that was so porous that the water passed right through. Coleman Ward, down at Mississippi Experimental Station, has grown golf greens on a mixture of sand and powdered rubber.

DR. PIERSON: We don't know whether we can take the rubber to completion, do we? Are there lines that we can use in respect to that use?

MR. DANNIS: The mere fact that we have a tilth improvement and do find a humus or humic action polymer-cementicious material, means that the action does not go to CO_2. I guess it is a residual hydrocarbon. But how long this lasts, I don't know.

CHAIRMAN McCORMICK: I would like to pose a question to either of these two panel members, perhaps a two-part question: Have either of you looked for volatiles rather than particulates, and if you have, have you made any attempt to identify the quantity? I raise this question because it has been suggested, as long as 15 or 20 years ago, that trace quantities of such volatiles as benzopyrene--which is a known human carcinogen--resulted from tire wear. Certainly it is also known that benzopyrene is present in our urban atmosphere, though whether it comes out of the exhaust pipe or from other sources has never been tied down completely. But at least it has been suggested that tire wear might be perhaps one source. Have you looked for it?

DR. PIERSON: You are not talking about a large part of the material balance. While we have shown nearly all the material comes off in particulates, we still haven't answered your question yet. You answer it.

MR. DANNIS: No, I haven't looked for a polymer. I have had hydrocarbons coming from the gas phase.

CHAIRMAN McCORMICK: I did; I had help again from Kriskey. We literally cooked some rubber on a hot plate and were trying to examine the vapors; we couldn't find anything. We came to the conclusion that the nose is more sensitive than our results. We just got a characteristic odor of burning rubber; that was easily identified.

DR. CARL A. NAU (Texas Tech University, Lubbock, Texas): I take it that all of us here are interested in the health aspects of the rubber particulates, and on this basis I would like to make a few comments based on studies I was involved in over a period of 8 years. We started in 1964. We collected material in the Holland-Lincoln tunnel and in indoor parking areas. We were never able to collect any particulates in ambient air. (I appreciate very much the papers this morning.) We wanted enough material so that we could expose primarily the rhesus monkeys to rubber particulate in the air that they were breathing. You know by this time that I feel that environmental factors can adversely affect human health. How do we get enough of the particulates?

We went to the Bureau of Standards where they have, or did have, abrasion testing machines that they could run. We got one with various angles and one with various pressures on the road and they rated the tires, but we then discovered that they had dusted the road with talc. Now we had tire dust with talc, which we didn't want. So we wasted a lot of money to get this.

Then we went to the tire recap places and got the abrasions. We were able to get the help of the Cabot Research people in Boston. We shipped them this abrasive material and they froze it with liquid nitrogen and micronized it. We got a significant amount of material, less than 5 microns in diameter, which we used for inhalation studies.

Then we used guinea pigs and rhesus monkeys for 8 years, the monkeys over 8 years, the guinea pigs for their lifetimes. We found that we had a lot of trouble with guinea pigs because they huddled together and put their noses in each others fur; this served as a good filter. That shows you how we have methods of protecting ourselves, just as the animals do.

We also found from our monkeys that the cleansing potential of the monkey pulmonary system was fantastic. We couldn't get rubber dust into the monkey lungs, but we thought we ought to get in. It either went in and out or the cleansing mechanism was quite good. We did this over an 8-year period of time, 7 hours a day, 5 days a week, and we used high concentrations (I'm afraid to mention numbers, but I think in terms of 0.6 of a milligram per cubic foot). We never published this; it was in '64. I made some trips to Akron and to New York to elicit some interest in our proposed study. It was ineffectual and I could not arouse any interest in it. So we went on our own, because some of the people who were talking about air pollution--I won't mention any names--inferred that rubber dust was not a potential pollution problem.

So we studied these monkeys and we got all the things that I told you about yesterday--electrocardiograph, X-ray films and we did pulmonary function studies, etc.--and we came to the conclusion that particulates of rubber in the air as an ambient air pollutant is not really that important a problem.

We had monkeys of both sexes being exposed to rubber dust. Some became pregnant, and we let them continue their pregnancies to full term and delivery. Then we exposed the newborn to the same rubber dust, and we studied the infants as they grew older.

CHAIRMAN McCORMICK: Thank you, Dr. Nau, for your enlightening remarks. I think a question is coming in from the audience.

MR. BOBBY D. LaGRONE (U.S. Rubber Reclaiming Co., Inc., Vicksburg, Mississippi): I have a question for Dr. Nau, regarding the negative information. We agree or confess that we (U.S. Rubber Reclaim) supported the work that was done down at Mississippi State University. We were hoping to be able to modify the soil by use of the physical amendment that would be imparted by the rubber. For instance, you did not have to aereate the golf range each year. In regard to field crops, you did not have a problem with crusting. That worked very well, but we use 30-mesh, not 100-mesh material. We found that the rubber crumb had a phytotoxic effect on most plants; it wasn't so severe for turf grass, but was severe on soy beans, wheat, and this sort of thing.

DR. NAU: Cucumbers?

MR. LaGRONE: It was very bad in cucumbers, that's for sure. We finally concluded that it was the zinc oxide that was causing most of the problems. I am more or less inclined to agree with Dr. Pierson's statement that rubber ground from the tire is of a very fine nature, because the material that we used was there after 2 or 3 years, actually about 4 years now.

CHAIRMAN McCORMICK: Alright, now there was a question down here.

MR. JOSEPH LAMAN (Firestone Tire and Rubber Company, Akron, Ohio): Since the subject of biodegradation was brought up in relation to this disposal of tires, Firestone embarked on a meaningful program to employ biodegradation to recycle valuable chemicals back to production cycle. The result of this work was the recovery of carbon black, which is a gut raw material of the rubber producing industry. I have with me today our Dr. Kay and Dr. Crane, who directed this work; I was wondering if they would care to comment on the results of your work?

DR. ED L. KAY (Firestone.Tire and Rubber Company, Akron, Ohio): I would like to substantiate the fact that accelerator tridents and zinc oxide were toxic to the microbes feeding on the rubber itself. We weren't able to carry it to completion, although we did do some test work. I think that sums it up.

[Following are supplementary comments provided by Dr. William Pierson in his letter of March 20, 1975, to Franklin Ayer, conference coordinator, Research Triangle Institute, Research Triangle Park, North Carolina.]

As for supplementary comments, I wish to submit the following. It has to do with the two rubber-tire-wear air-pollution papers on Thursday morning by Mark Dannis and me. Both of us were careful to indicate the disagreement between us on the size distribution of airborne tire-wear-debris particles. At high-speed cruise conditions, I found that some 60 wt percent of the airborne tire debris was in the particle-size range <1.1μm, whereas Mark Dannis reported that particles smaller than 3μm were essentially nonexistent under comparable conditions. I would like to offer one possible explanation, as follows. If the sub-1.1μm airborne tire debris found by us at high-speed cruise predominantly consisted of particles smaller than the wavelength of light (i.e., smaller than ~0.3μm), then Mark Dannis would have missed them because his analysis depended upon optical microscopy. If this explanation is correct, it would imply that his tire-debris totals are too low.

An alternative possible explanation is that losses in our HiVol cascade impactor, which we know to have occurred, may not have affected all sizes equally but rather affected primarily the larger ones. Judging by the amounts of tire debris collected on concurrently running gross impactors, it would still turn out that at least 20 wt percent of the tire debris was in particles smaller than 1.1μm.

It is possible that both explanations are valid to some extent. Other alternatives are not apparent. For example, road surface probably can be ruled out; though the measurements in our case involved only asphalt surfaces, Mark Dannis did measurements involving several types of roadways with qualitatively similar results with respect to size distribution.

ENVIRONMENTAL ASPECTS OF RECLAIMING AND RECYCLING RUBBER

Bobby D. LaGrone and Edward A. Gallert*

Abstract

The value of recycling waste rubber back into the process was recognized very early and for all practical purposes, the rubber reclaiming industry started shortly after 1844, the year that Charles Goodyear obtained his patent on vulcanization of rubber with sulfur.

By today's standards the early reclaiming processes were quite crude and although millions of scrap tires have been removed from the landscape, the effect of the reclaiming industry (either positive or negative) on the environment was not given any appreciable consideration until the past few years.

Practically all of the reclaimed rubber used in the past (and at present for that matter) has been used as the result of processing and economic considerations. The move toward improving our environment has to this date actually had a negative effect on the reclaiming industry. Several reclaim plants have actually closed their operation rather than commit the necessary capital to bring them up to a standard where they would meet EPS air and water quality guidelines. This has resulted in a lesser amount of scrap rubber being reclaimed at a point in time when its disposal is becoming more critical.

Those companies who remain in the reclaimed rubber business obviously feel that they can operate their plants within EPA regulations and at the same time contribute substantially toward winning the ecology battle by using waste tires as their basic raw material.

Those of us in the reclaiming industry have always looked upon waste rubber as a badly neglected potential national resource and have endeavored to develop methods to recover and reclaim the rubber so that the unique properties of the rubber can be fully utilized. Simply "getting rid of scrap rubber" has never been and is not presently a motivating factor in the use of reclaimed rubber.

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*Bobby D. LaGrone, Vice President - Technical; Edward A. Gallert, Vice President - Planning; U. S. Rubber Reclaiming Co., Inc., Vicksburg, Mississippi.

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We are very much aware of the fact that at best only about 10 percent of the scrap rubber generated each year can be reused back into conventional rubber compounds. Unfortunately the more stringent requirements of tire compounding today (especially radial tire compounding) has resulted in a substantial reduction in the normal demand for reclaimed rubber. This has led us to research other areas where the unique properties of waste rubber can be used to advantage.

Areas that we have researched that show potential for utilizing substantial quantities of waste rubber and appear to be economically feasible on a cost performance basis are: recreational surfaces, rubberized asphalt joint sealers, rubberized asphalt for chip sealing highways and for use as the binder for hot-mix asphalt concrete and plant mix friction seals, in bridge seal and roofing membranes, and as a strain relieving interlayer for prevention of reflection cracking asphalt concrete overlays.

All of these systems have been tested in the field and any one of several of these methods would accomodate all of the approximately 10,000,000,000 pounds of waste rubber generated each year.

Introduction

The value of recycling waste rubber back into the process was recognized very early and for all practical purposes, the rubber reclaiming industry started shortly after 1844, the year that Charles Goodyear obtained his patent on vulcanization of rubber with sulfur (ref. 1).

The early reclaiming processes were quite crude with regard to environmental control aspects and most plants would probably have been refused an operating permit under today's regulations.

What Is Reclaimed Rubber?

Reclaimed rubber is described by Ball in the manual of Reclaimed Rubber as "the product resulting from the treatment of ground vulcanized scrap rubber tires, tubes, and miscellaneous waste rubber articles by the application of heat and chemical agents whereby a substantial devulcanization or regeneration of the rubber compound to its original plastic state is effected, thus permitting the product to be processed, compounded, and revulcanized" (ref. 2).

The Reclaiming Process

In most of the early reclaiming processes, chemicals used in fiber removal were the prime source of pollutants. The fiber was removed or "digested" by the use of acid or sodium hydroxide in relatively high concentrations (up to 7 percent). After World War II, the use of SBR rubber became widespread, and reclaim produced by the old "alkali" process became very hard during the digesting cycle. A neutral digester process was then developed using either clear water or metal chloride (zinc or calcium) for the removal of fiber.

In both the "Neutral" and "Alkali" Digester processes, the cracked vulcanized rubber was added to the digester along with devulcanizing agents and processing oils. The so-called "active agents included xylyl mercaptan, dixylyl disulfides, dodecyl mercaptan, and ditoyl disulfides. Only small amounts of these materials were used (generally less than 1 percent). The processing oils used were tall oil derivatives, pine tar, coal tar, petroleum and coal tar naphtha, etc.

After the rubber had been cooked in the digester for several hours, the digester was blown down and the softened rubber was washed, dried, and mixed with rubber compounds (carbon black, clay, Mr, etc.). The rubber, filler, and oils were masticated, passed through a refiner, strained, and then refiner sheeted.

The Digester process was widely used and modifications of this process are still in use today. Disadvantages of the old Digester process were that it required the removal of excess defiberizing agents and the salts formed as reaction products with the fibers. This is a difficult task and regulations imposed in our move toward improving the environment have prompted several companies to simply close down their operation rather than commit the necessary capital to bring them up to a standard where they could meet EPA air and water quality guidelines.

Those who have remained in the reclaiming business, have gone to a mechanical fiber separating system. This has helped to eliminate part of the problem; however, the problem of handling the oils and other chemicals that are not absorbed into the reclaimed rubber, and the zinc that is extracted from the waste rubber in processing, must still be dealt with.

Since another member of this panel is more familiar with the Digester processes being used today and the environmental problems that are being encountered with it, we will briefly review the mechanical (or Reclaimator) process used by our company and then address our attention to the positive effects of the reclaiming industry on the environment

The Reclaimator Process

A line flow diagram of the Reclaimator process is shown in figure 1. Tires are brought in from the field by scrap rubber dealers who are generally paid for removing them from service stations and tire dealers. They are thrown onto a belt (figure 2) and passed by a metal detector that rejects wire cord tires (figure 3). Wire cord tires could possibly be used for certain applications; however, since a considerable amount of reclaimed rubber is still used back into tires and since removing the fine wire is a very expensive process, they are not presently being used by reclaimers. Nevertheless, practical processes are on the drawing board for the reclaiming of these tires.

An old tire is a very tough piece of scrap and for a large scale operation, massive equipment is required to reduce it to small pieces. In our process, tires are passed through a two-roll cracker (figure 4) and recycled until the pieces pass a 3/4-inch screen. The high amount of recycle results in a very uniform blend. The bead wire is picked from the system by hand (figure 5) and a magnetic separator system removes smaller pieces of wire and other tramp metal. This material is presently disposed of in a land fill and several alternatives for using it are being studied.

The blended "cracked stock" is conveyed to a fiber separator system where it is passed through a series of hammer mills, slow speed beaters, and air elutriation equipment to separate the fiber from the "ground rubber." The fiber is baled (figure 6) and can be used for a variety of products although its value is still primarily that of a stuffing material.

The "separated stock" (figure 7) is then passed to a fine grinding system (figure 8) where the vulcanized rubber is screened and ground to the desired mesh size. It is still in the vulcanized state at this point and some "ground rubber crumb" (after being passed over an "air flotation stoner" to remove nonmagnetic and/or nonmetallic contamination) is suitably packaged and sold for a variety of uses. The ground rubber has found wide acceptance as a resilient filler in applications such as athletic surfaces for track and tennis and it is this form of recycled rubber aggregate that we use in our Strain Relieving Interlayer for reducing reflection cracking in asphalt paved roads. This application for waste rubber will be discussed in greater detail presently.

The next step of the reclaiming process requires heat, pressure, and chemical modification to soften the rubber and break enough of the cross-linked chains (figure 9) to again make it millable and vulcanizable. The ground rubber crumb (normally 30 mesh is used to produce reclaim) is mixed with reclaiming chemicals and fed to the Reclaimator which is a heavy-duty screw device that subjects the rubber/oil mixture to a very high temperature and pressure (figure 10). Note that no water or steam is added to the rubber in the process. However, some of the lighter fractions of the reclaiming oils are driven off in the Reclaimator and this along with the steam evolved when water is added to cool the hot stock coming from the Reclaimator results in a steam mist containing approximately 2 percent of the hydrocarbon gasses. We have, in years past, simply vented this mist to the atmosphere; however, due to its pungent odor, we now condense the material and scrub the final emission to obtain a clear stack. An oil/water separating system is used to clean up the water that is condensed and collected from the scrubbers. The only real problem we have had in treating this water has been in reducing BOD and organic nitrogen levels.

Reclaimed rubber coming from the Reclaimator process is essentially equivalent to that coming from a Digester and the same types of chemicals are used. It is softened to the point where it can be milled, is vulcanizable, and is relatively soluble in asphalt. It can be either sheeted, baled, or dusted with a parting agent to produce a powdered product for use in asphalts (figure 11).

Positive Effects of Reclaiming

Those of us in the rubber reclaiming industry have always looked upon waste rubber as a badly neglected potential national resource and have endeavored to develop methods to recover and reclaim the rubber so that its unique properties can be fully utilized. Simply "getting rid of scrap rubber" has never been and is not presently a motivating factor in the use of reclaimed rubber.

Advantages of Reclaimed Rubber in Rubber Compounding

Practically all of the reclaimed rubber used in the past (and at present for that matter) has been used as the result of processing and economic considerations.

We can list the advantages in the use of reclaimed rubber in conventional rubber compounding as follows:

a. Assists the breakdown of raw polymers;
b. Assists to uniformly disperse pigments;
c. Incorporates fillers and softens faster with less power use;
d. Extrudes and calenders faster with better adherence to shape and gauge because it has less nerve than virgin polymers;
e. Has less tendency to deform during shelf aging and open stream curing;
f. Has a tendency to stabilize curing systems because reclaimed rubber is not sensitive to overcures;
g. Results in overall cooler processing;
h. Results in fewer mold defects such as blisters, trapped air pockets, and back-rinding;
i. Imparts good building tack;
j. Price has been very stable throughout the years and on parity basis compared to SBR is a better buy today than ever before.

Due to some or all of the reasons stated above, reclaim rubber has been used by the rubber industry almost since its inception. Some articles are made of all reclaimed rubber; however, most compounds utilize reclaimed rubber in a blend with virgin polymer.

The reclaiming industry has by virtue of its normal operation consumed from 5 to 10 percent of the waste rubber generated through the years and has, without a doubt, had a very beneficial effect on the overall environment by removing millions of tires from the landscape. The problem of disposing of waste tires would have been an even greater problem long before now had it not been for the reclaiming industry.

Recent developments such as the introduction of the radial tire, which uses little if any reclaim rubber, and the closing of several reclaim plants, due to economic and environmental pressures, has substantially reduced the quantity of reclaim consumed in this country at a time when the ecological problems associated with waste rubber are mounting.

There were 182,600,000 passenger tires and 35,590,000 truck tires shipped in 1974 (ref. 3). This is down slightly from the 201,590,000 and 36,878,000 figures for 1973; however, it is believed to be a temporary trend, and the outlook is for increased tire production in the future. This is in itself a formidable pile of scrap, but when you consider that it constitutes only approximately 64 percent of the total rubber compound produced each year, it is easy to see the magnitude of the problem we are facing in solving the waste rubber disposal problem. The reclaim industry produced 330,000,000 pounds of rubber in 1974, yet probably consumed no more than 4 percent of the waste rubber generated. This equates to approximately 23,500,000 tires that were removed from the landscape during 1974 as a result of reclaiming.

From the data presented above it is quite obvious that large scale uses for waste rubber must be found. After years of researching many possibilities for using waste rubber, it is our view that the most promising area in which to utilize the unique properties of the rubber to economic advantage is highway construction and maintenance. Let me state here very emphatically that we are not simply suggesting that waste tires be "buried in the highways" (although, this too, might be a more worthwhile procedure than burying them in the ground). We are suggesting methods where they can be utilized to improve the performance and durability of our highways and result in an overall savings to society.

Other members of this panel will make their proposals for using scrap tires. We would like to apprise you of several of ours.

Proposals for Utilizing Waste Rubber in Highways

1. Rubberizing Asphalt Binders with Reclaimed Rubber

Powdered reclaimed rubber can be dissolved in compatible asphalt cements by cooking at elevated temperatures to produce rubberized asphalts with improved flexibility, temperature susceptibility, resilience, adhesion, and resistance to flow and brittleness.

Twenty percent by weight of powdered reclaimed rubber (Flo-Mix) is added to the asphalt cement and cooked at 400-425°F for 30 minutes to produce the rubberized binder which can be used for several highway applications. Table 1 shows typical effects of the powdered reclaimed rubber (Flo-Mix) addition to several grades of asphalts.

2. Joint and Crack Sealing

The rubberized binder can be prepared easily (on site) for this purpose using a conventional "tar kettle" (figures 12, 13, and 14). This gives the maintenance engineer a functional sealer at minimum cost and the extended life of the sealer more than pays for the additional cost of the rubber. This product and procedure has been commercialized and adopted in several States.

The following quote (ref. 5) by two prominent highway maintenance engineers tells how this material has proven its value on a cost performance basis. Quoting from the May 1973 issue of Thruway Intercom, Messrs. Cleary and Clark state that:

> "Use of the additive (reclaimed rubber) almost completely eliminated the lack of flexibility in winter and excessive flow in summer. It also increased the bond to the edges of the joint, and extended substantially the life of the sealant in the joints.
>
> "The effectiveness of the sealer was further dramatized by the fact that instead of sealing joints each year, the program is now on a two-to-three-year cycle."

3. Rubberized Asphalt Binder for Chip Sealing

The improved properties imparted to the binder by the addition of Flo-Mix reclaimed rubber also makes it an excellent chip seal binder. The rubberized binder can be used to improve performance and durability of single seal jobs as well as double bituminous treatments. The rubberized binder can be prepared and sprayed using a conventional asphalt distributor.

A small pilot unit has been used to place tests of this concept in nine States during the past two seasons with no installation problems whatever.

Up to 1500 gallons of the rubberized binder can be prepared in each batch, which is generally sufficient material for a substantial field test. The asphalt binder is transferred from the state storage tank or tanker and heated to 400°F (figure 15). The reclaimed rubber powder is added at the rate of 2 pounds/gallon of AC as shown in figure 16. We would anticipate that a more efficient method for preparing the rubberized binder could be developed for larger scale installations. However, for test purposes we simply pour the powdered rubber through a lump breaker while circulating the asphalt within the tank. The turbulence caused by the circulating pump will keep the rubber in suspension until it is sufficiently dissolved into the asphalt for spraying (figure 17). When the material is sprayed at the cook temperature as we have done to speed up the process, a considerable amount of smoke is produced. However, it is no worse than regular AC if sprayed at comparable temperatures. We are studying the possibilities of emulsifying this material, which would make its application more convenient and eliminate the smoke.

These tests are being followed closely and a notable improvement in reduction of cracking was observed on a number of the tests after the first winter of service.

4. Flo-Mix Rubberized Asphalt as the Binder for Hot-Mix Asphalt Concrete

Flo-Mix rubberized asphalt can be used as the binder in regular hot-mix formulations to improve both hot and cold weather properties of pavements. Improved adhesion, flexibility, and temperature susceptibility of the binder results in a pavement with increased cold tensile strength and ability to yield under loading without fracture. Dr. Oaks of Mississippi State University (ref. 5) as well as other independent researchers (refs. 6,7) have substantiated these claims in their laboratory evaluations of rubberized AC. The energy absorbing, resilient properties imparted by the rubber also resist postcompaction problems such as bleeding, rutting, and shoving in hot weather (table 2).

The Flo-Mix rubberized asphalt is added at the hot-mix plant in the same manner as regular asphalt cement. For field tests the rubberized binder prepared in a distributor can be pumped directly to the hot mix plant as shown in figure 18. No change in the mixing operation is necessary. Standard tests should be made to determine optimum level for this type binder. Recent inspection of a test using this technique was made and there were no cracks in the section containing rubberized AC vs 30 for a control section after 1-1/2 years of service.

5. Flo-Mix Rubberized Asphalt as Binder for Plant Mix Friction Seals

The improved properties of the Flo-Mix binders make them especially well suited for use in open graded mixes such as the plant mix friction seals that are gaining in popularity as skid resistant overlays. The use of Flo-Mix binders in these mixes improves flexibility and resistance to brittleness at low temperatures while the increased viscosity of the binder reduces drainage during placement and hot weather service. Higher than normal mix temperatures are also possible with the Flo-Mix binder, which result in better stone coating and reduce possibility of stripping without reducing the binder film thickness.

The improvements in elasticity and cold tensile strength are illustrated in figure 19, which is a graphical representation of the stress-strain properties of a typical plant mix seal during the split cylinder tensile test.

Improved cohesion and resistance to drainage are shown in figure 20.

Any of these methods would use substantial quantities of waste rubber. At the suggested binder content, approximately one tire would be consumed/ton of hot mix prepared. To give some idea of the magnitude of this potential use for waste rubber, there were 5.6 MM tons of hot mix produced in the small State of Mississippi in 1974. This would have consumed 6,000,000 waste tires in this one application alone.

General Applications Flo-Mix Rubberized Asphalt

Flo-Mix rubberized asphalt can be utilized for other highway construction and maintenance jobs such as patching and waterproofing of bridge decks where improved flexibility and temperature susceptibility of the asphalt cement are desired. This concept is currently being field tested, but no definite evaluation has been made to date. An application procedure of this system is illustrated in figure 21.

SRI-Strain Relieving Interlayer for Arresting Reflection Cracks in Asphalt Concrete Overlays

In addition to utilizing "reclaimed rubber" to improve highways, we have also developed one large potential use for ground vulcanized rubber.

This is as a Strain Relieving Interlayer to prevent reflection cracking of asphalt concrete overlays.

The "SRI" is an elastic asphaltic composition composed of approximately equal parts by volume of a vulcanized rubber aggregate, mineral aggregate, and an asphalt binder. When applied in a thin layered membrane over surfaces prone to cracking, it forms a waterproof, strain-absorbing interface that will prevent base cracks from reflecting though to the surface to an asphalt concrete overlay.

The rubber and mineral aggregates are preblended, (figure 22) mixed with asphalt emulsion, and applied as a slurry using conventional slurry sealing equipment (figure 23). Curing characteristics are similar to regular slurry mixes, and temporary traffic can be allowed on the SRI in the interim period between its application and application of an asphalt concrete overlay (figure 24). The SRI is not formulated to be a wearing surface and the rubber aggregate will be pulled out of the layer if it is not overlayed within a relatively short time. The wearing surface should be four to six times the thickness of the SRI layer to prevent excessive strain from developing in the surface course.

It has been found that a 1/4- to 3/8-inch Strain Relieving Interface will effectively accommodate base movement of as much as 0.25 inch without having cracks reflect through the surface course (figure 25). This method is especially desirable when excessive thickness of pavement is not practical or cannot be used due to loss of curbs, etc.

This concept has been approved by the Federal Highway Administration for testing under the NEEP program and tests are now under evaluation in several States. Figure 26 shows the effectiveness of the SRI to arrest cracking after a 3-year test period. A recent report by the Vermont Highway Department (ref. 8) indicated that a reduction in reflection cracks from 43 percent to 7 percent was achieved by use of this type system. Roughly 3,000 scrap tires would be consumed for each lane mile of highway constructed using this technique.

Economics

Obviously, the use of reclaimed rubber will increase the cost of the project when compared to simple aggregate-asphalt mixtures. This can be justified if only a slight extension in service life is obtained.

The following estimates are based on average construction costs in Mississippi. The amounts for the Strain Relieving Interlayer are derived from a test project, and the cost of using the rubber is somewhat higher than if it were used in general practice.

Type of construction	Percent increase in project cost due to rubber	Pavement lifetimes to justify use of rubber
Rubberized binder in asphalt concrete (resurfacing)	5.5	1.06
Rubberized binder in chip seals	28.2	1.28
Strain Relieving Interlayer	14.8	1.15

These data, of course, do not include the value of the removal of the waste tires from the environment nor a reduction of inconveniences caused by having to repair the surface more frequently.

Summary

In summary we have proposed several methods for improving highway performance and durability where rubber derived from waste tires can be recycled back into the highway system.

It has been demonstrated that no special equipment is necessary to utilize reclaimed rubber as suggested in these proposals. We can foresee no unsolvable engineering or supply problems in producing these materials on a larger scale.

As with most any other additive, use of rubber in asphalts and ashpalt concrete pavements will invariably increase the initial cost of the job. However, when cost performance data are taken into consideration, economics of the proposed systems appear very favorable.

We suggest that serious consideration be given to utilizing this "wasted solid" rubber to improve our streets and highways where it is generated, and by so doing, create a new National resource, conserve present resources, and finally eliminate an ever-increasing costly ecological problem.

REFERENCES

1. E. F. Sverdrup and B. R. Wendrow, "Rubber Reclaiming," Encyclopedia of Polymer Science and Technology, Volume 12, 1970.

2. J. M. Ball, Manual of Reclaimed Rubber, The Rubber Reclaimers Association, Inc., 1956.

3. "Review 1974 - Preview 1975," Rubber Age, January 1975.

4. T. M. Cleary and W. C. Clark III, "How Your Old Tires Windup in the Thruway," The Thruway Intercom, April, May 1973.

5. D. T. Oaks and W. D. McCain, Jr., "Improvement in the Durability of Asphalt Pavements," Engineering and Industrial Research Station - Petroleum Engineering, Mississippi State University, March 1973.

6. Jack E. Stephens and S. A. Mokrzewski, "The Effects of Reclaimed Rubber on Bituminous Paving Mixtures," Civil Engineering Department.

7. Donald E. Carey, "A Laboratory Evaluation of Rubber-Asphalt Paving Mixtures," Research Report No. 79, Research Report No. 72-10B (B), Louisiana HPEI (11), Louisiana Department of Highways.

8. J. T. Gray, E. H. Stickney, and A. W. Lane, "Reducing Reflection Cracking in Bituminous Overlays Utilizing a Strain Relieving Interlayer of Rubberized Slurry," Initial Report 74-3, May 1974, Vermont Department of Highways.

Table 1. Effects of powdered reclaim rubber in Colorado asphalts

Type asphalt	Sinclair	Sinclair	Frontier	Frontier	Conoco	Conoco
Treatment	Control	Rubber	Control	Rubber	Control	Rubber
Softening pt.	108	111	106	118	103	116
Penetration:						
39.2°F	26	52	46	54	40	52
77°F	121	154	155	138	136	134
Pen. ratio	21.5	33.8	29.7	39.1	29.4	38.8
Flow @140°F, cm/hr	33	18	29	11	33	11
Cold bond @0°F	F-1 Brittle	5 OK	F-1 Brittle	5 OK	F-1 Brittle	5 OK
Plant mix seal:						
Elastic yield @0°F	0.073	0.087	0.055	0.086	0.054	0.088
Tensile @0°F	51	93	54	95	45	80

Table 2. Effects of reclaim rubberized asphalt in asphalt concrete pavements

Type binder	150-200 Pen.				40-60 Pen.	
Treatment	Control		Rubberized		Control	Rubberized
Binder level	7.0	7.5	7.0	7.5	7.0	7.0
GTM test @140°F:						
GTM stability index	1.03	2.57	1.00	1.03	1.60	0.71
GTM strength index	1.70	1.03	1.43	1.28	1.41	1.43
Density (γ_A* @ 200 cycles) #/cu. ft.	133.5	135.0	129.6	130.8	134.7	130.7
Cold tensile @0°F	497	599	549	606	491	593+†

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*γ_A = Density based on aggregate only to correct for binder differences.

†At capacity of loading device.

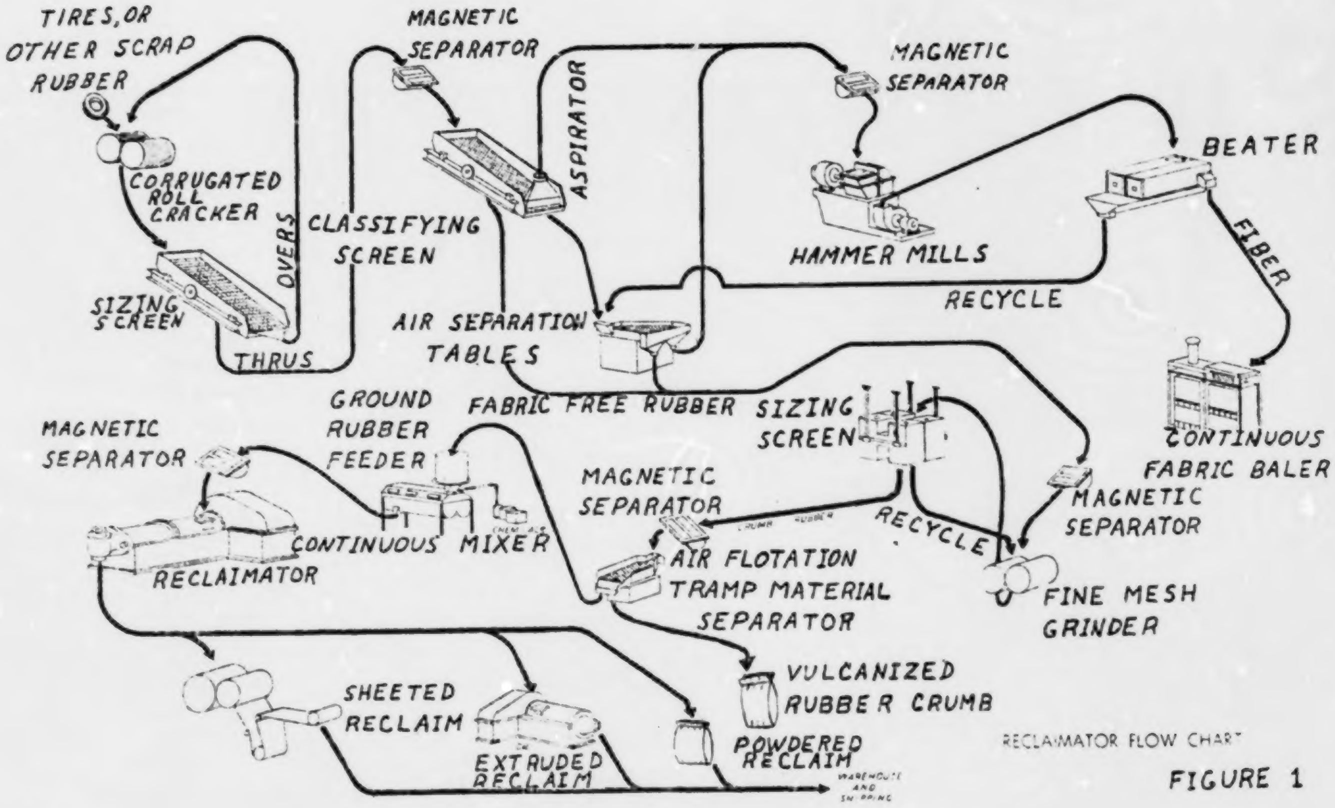

TIRES, OR OTHER SCRAP RUBBER
CORRUGATED ROLL CRACKER
SIZING SCREEN
OVERS
THRUS
CLASSIFYING SCREEN
MAGNETIC SEPARATOR
ASPIRATOR
AIR SEPARATION TABLES
MAGNETIC SEPARATOR
HAMMER MILLS
BEATER
FIBER
RECYCLE
CONTINUOUS FABRIC BALER
FABRIC FREE RUBBER
SIZING SCREEN
GROUND RUBBER FEEDER
MAGNETIC SEPARATOR
CONTINUOUS MIXER
RECLAIMATOR
MAGNETIC SEPARATOR
CRUMB RUBBER
RECYCLE
MAGNETIC SEPARATOR
AIR FLOTATION TRAMP MATERIAL SEPARATOR
FINE MESH GRINDER
VULCANIZED RUBBER CRUMB
SHEETED RECLAIM
EXTRUDED RECLAIM
POWDERED RECLAIM
WAREHOUSE AND SHIPPING
RECLAIMATOR FLOW CHART
FIGURE 1

Figure 1. Reclaimator flow chart.

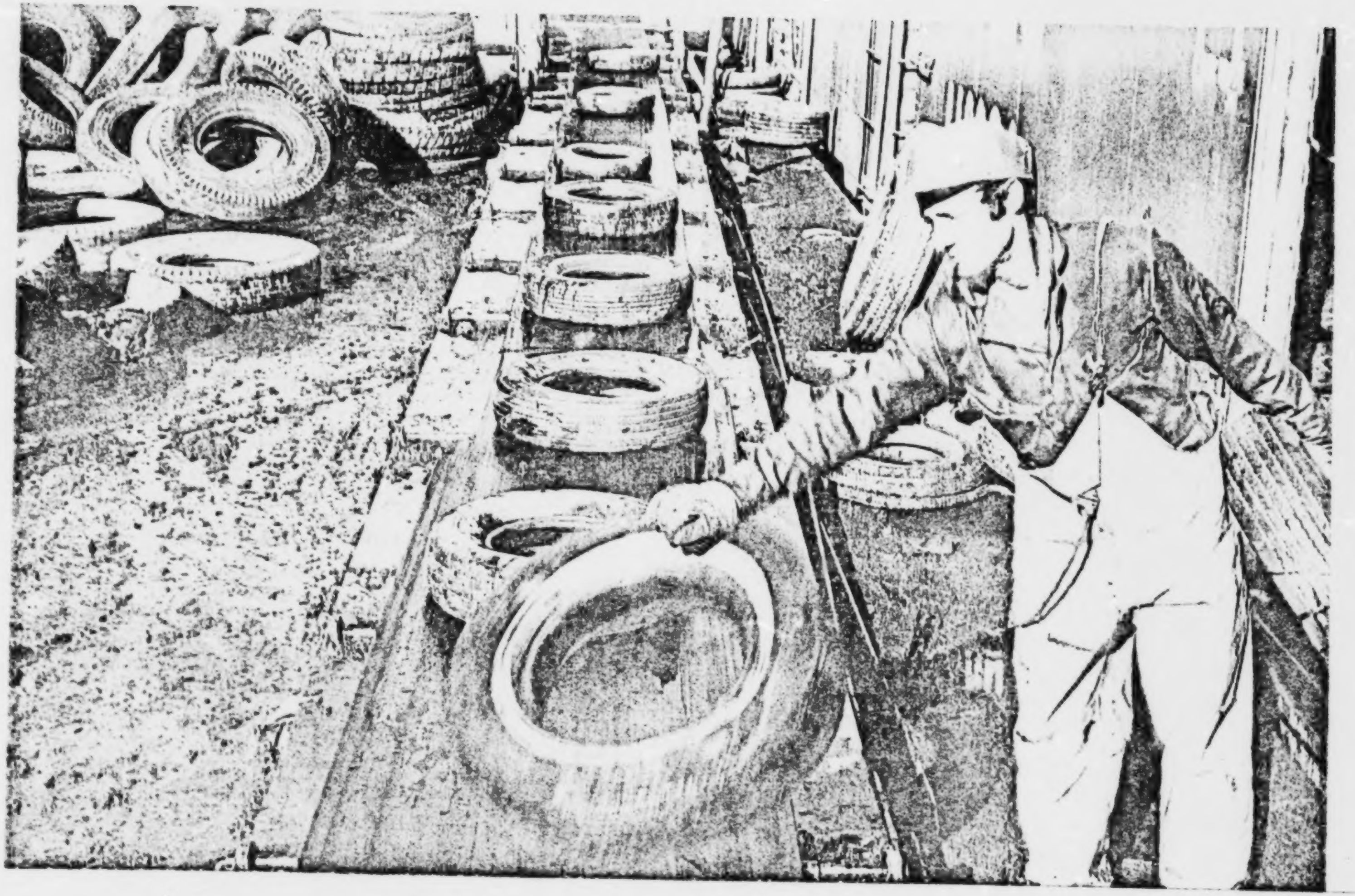


Figure 2. Unloading scrap tires.

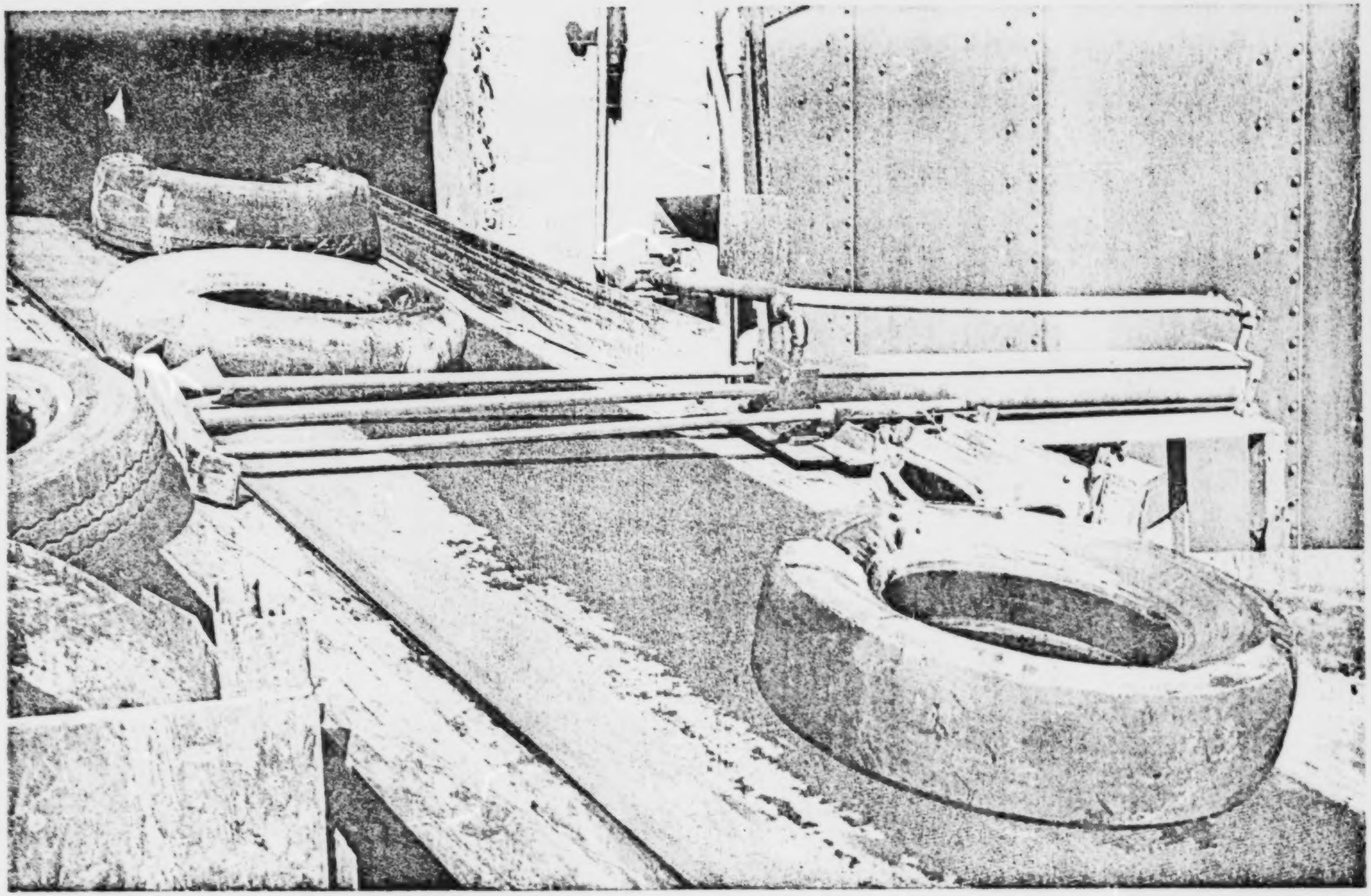


Figure 3. "Frisker removing steel belted tire from the system.

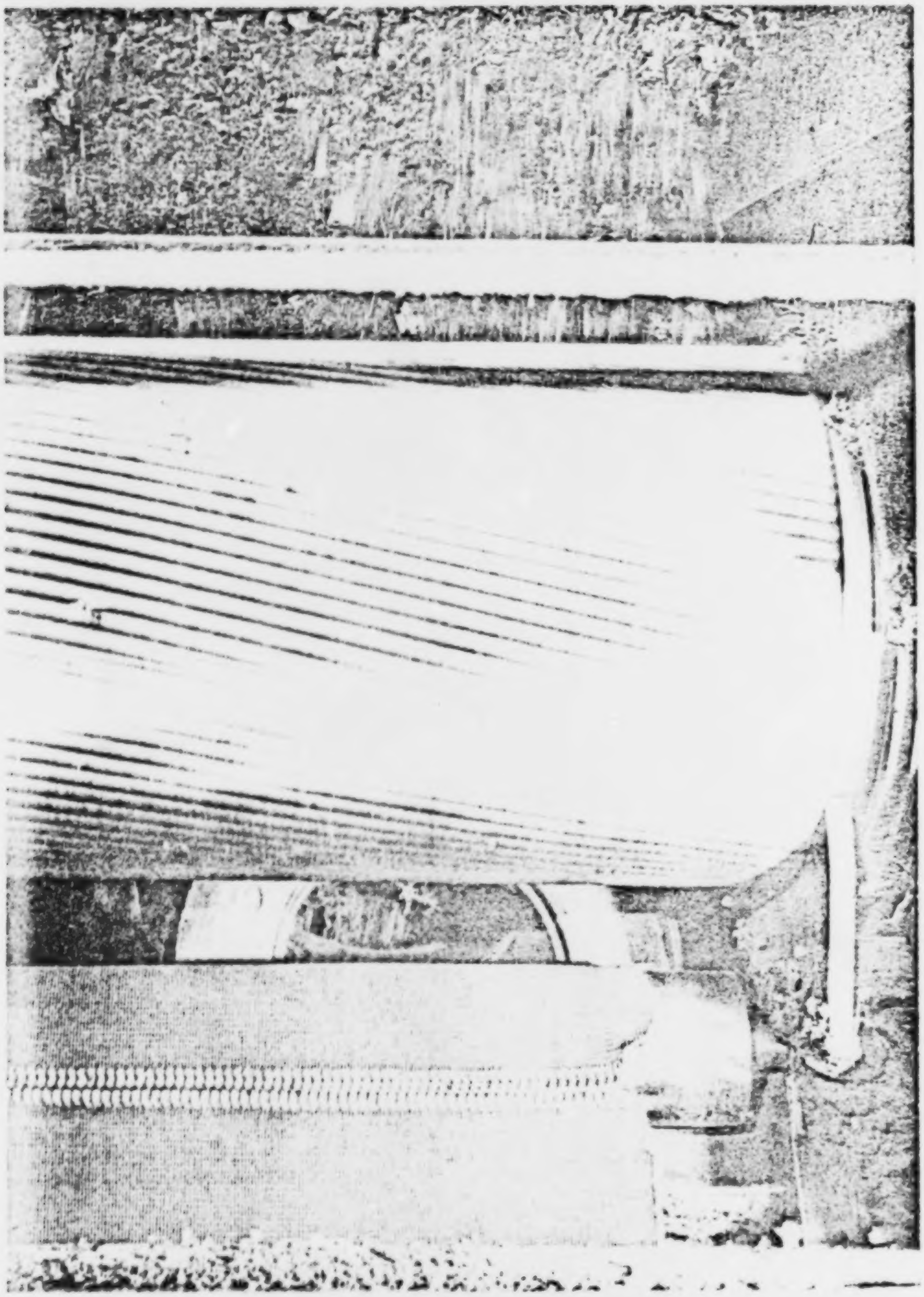


Figure 4. Cracker.

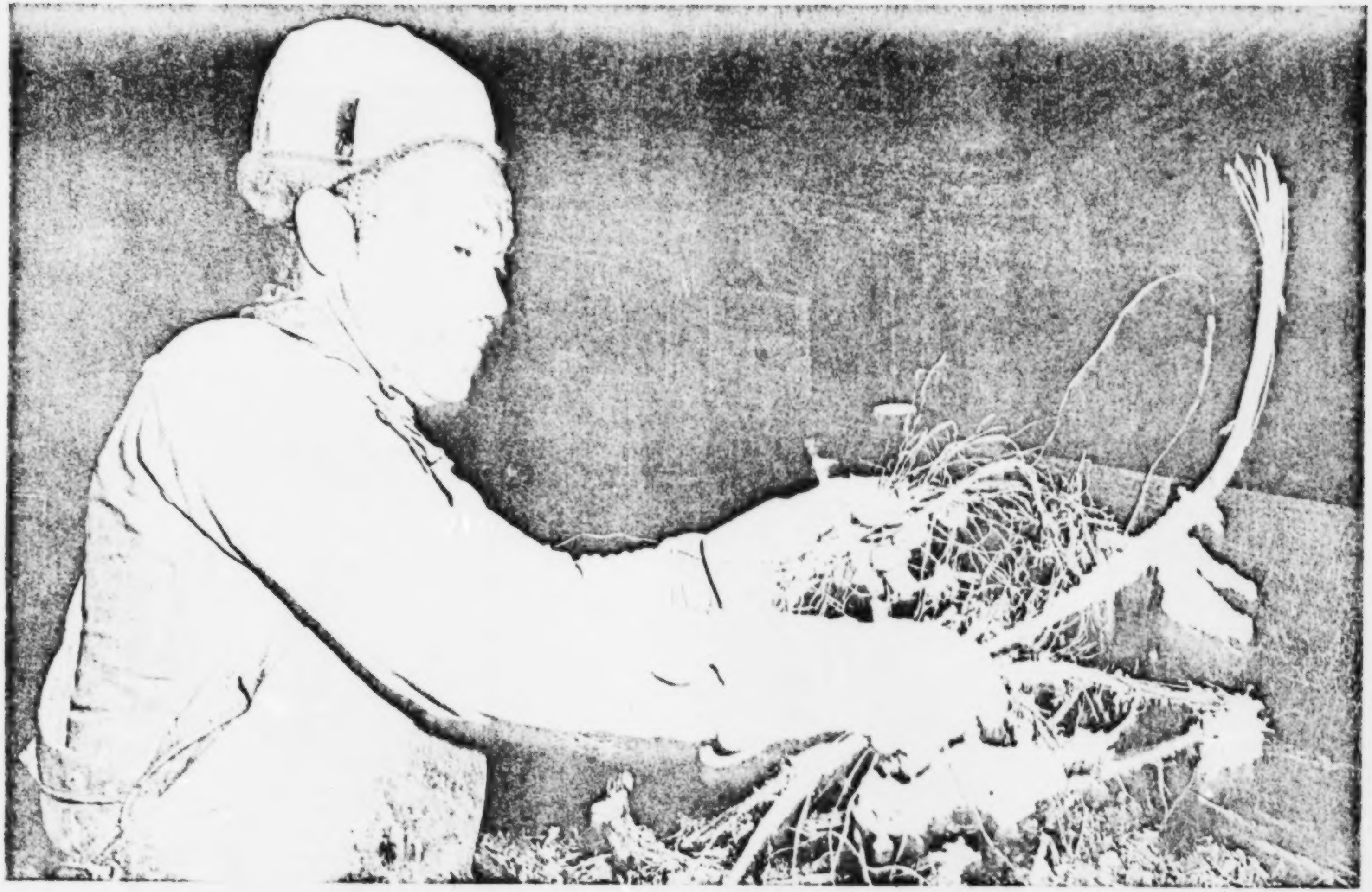


Figure 5. Removal of bead wire.

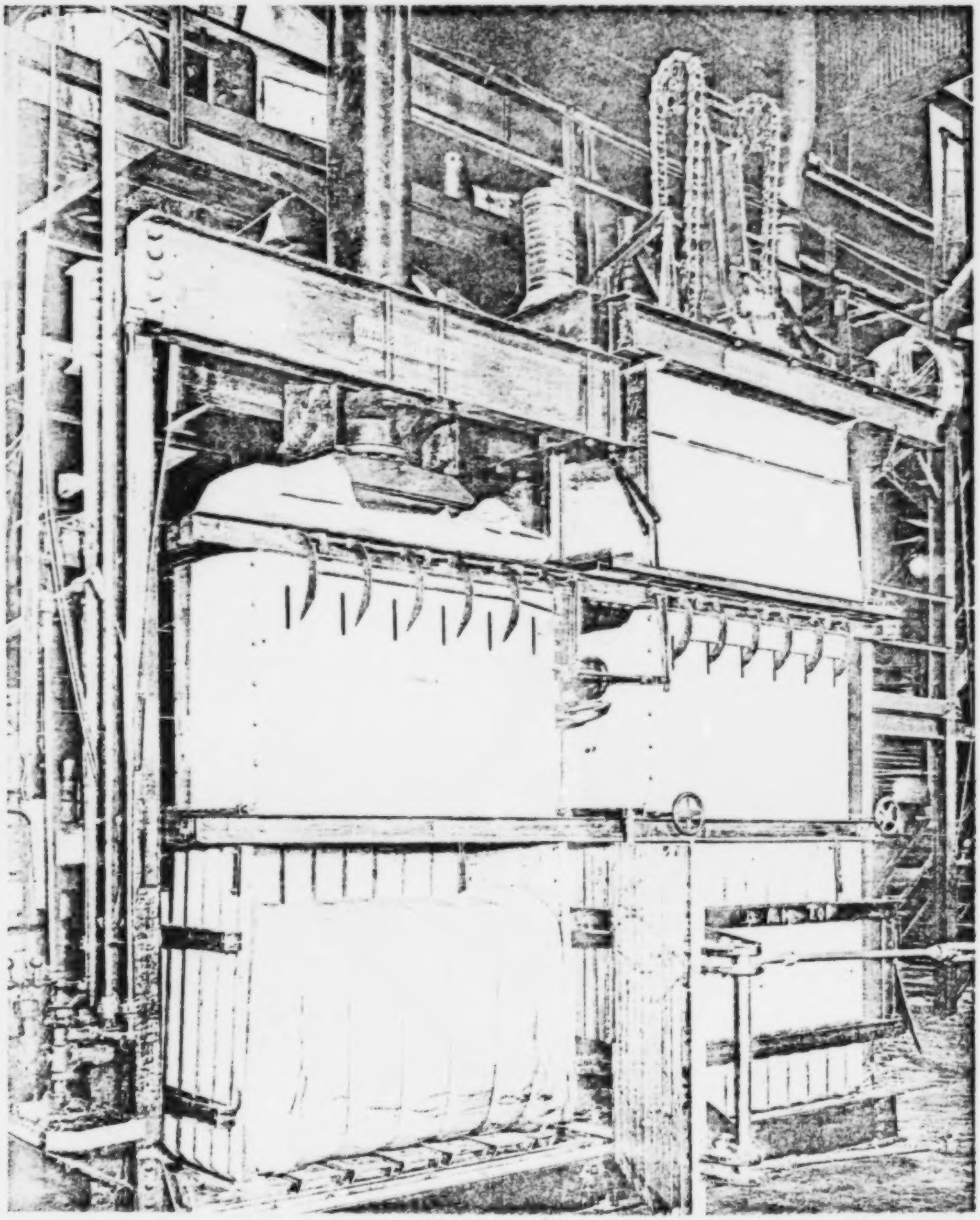


Figure 6. Baling of fiber.

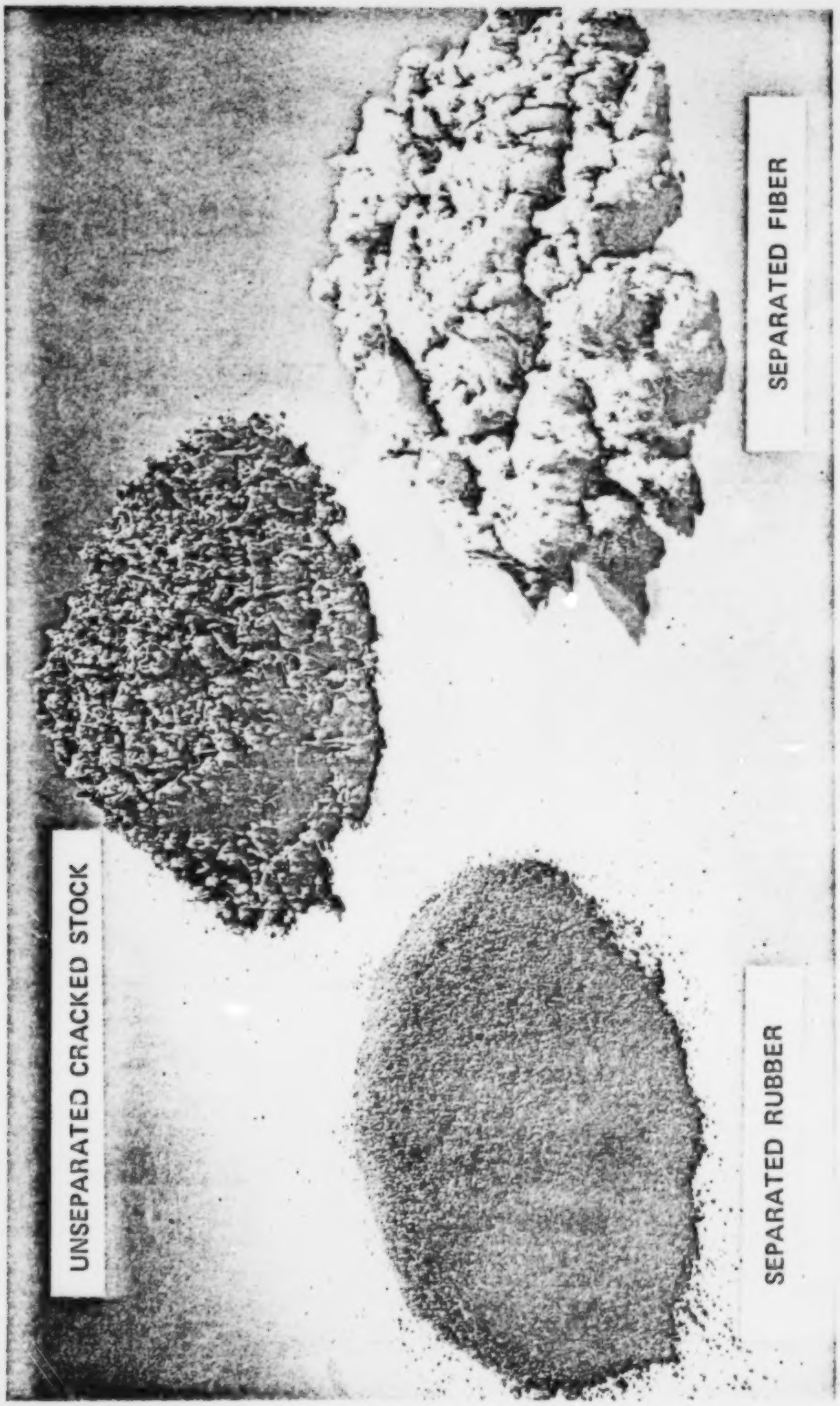

UNSEPARATED CRACKED STOCK
SEPARATED RUBBER
SEPARATED FIBER

Figure 7.

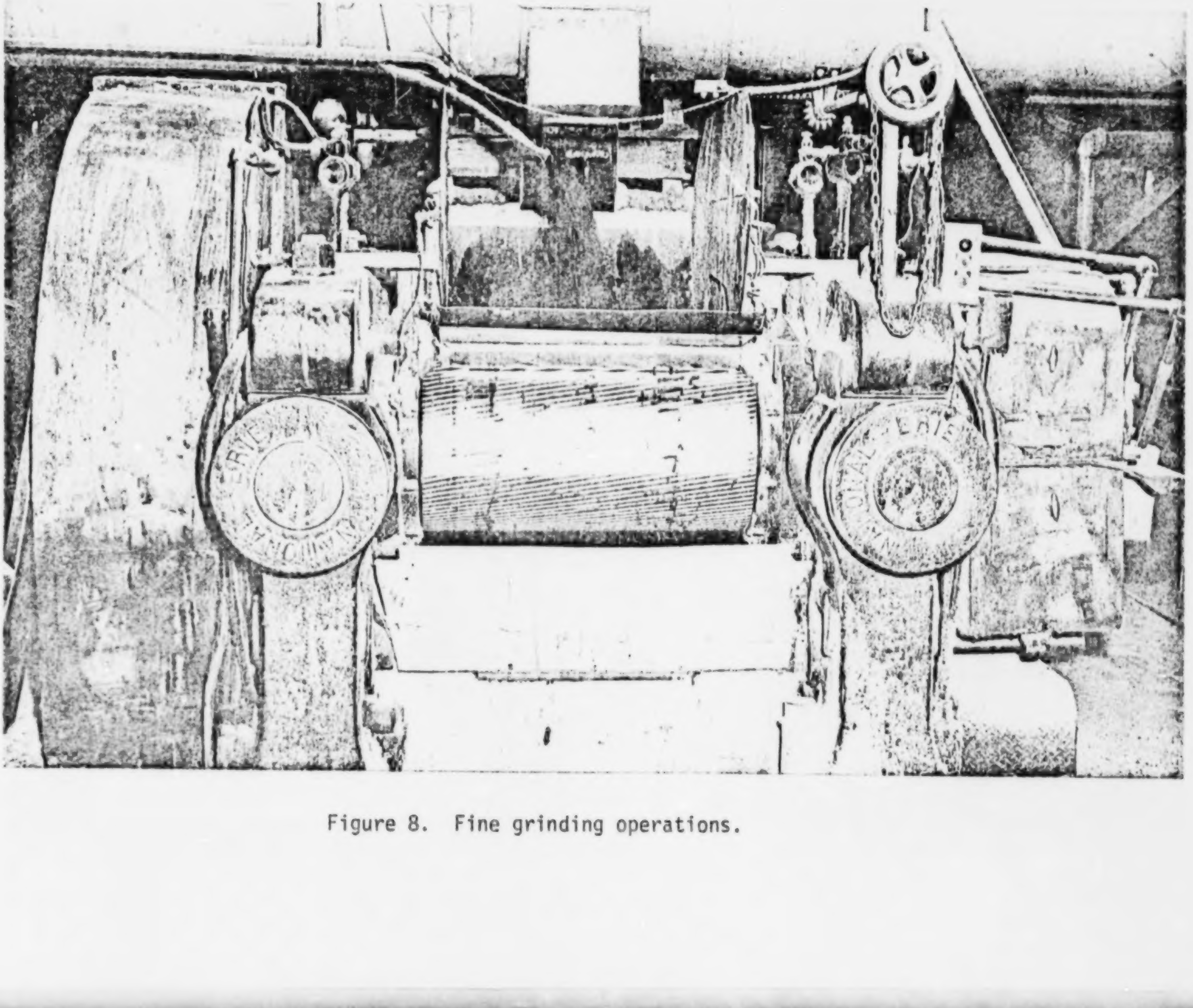


Figure 8. Fine grinding operations.

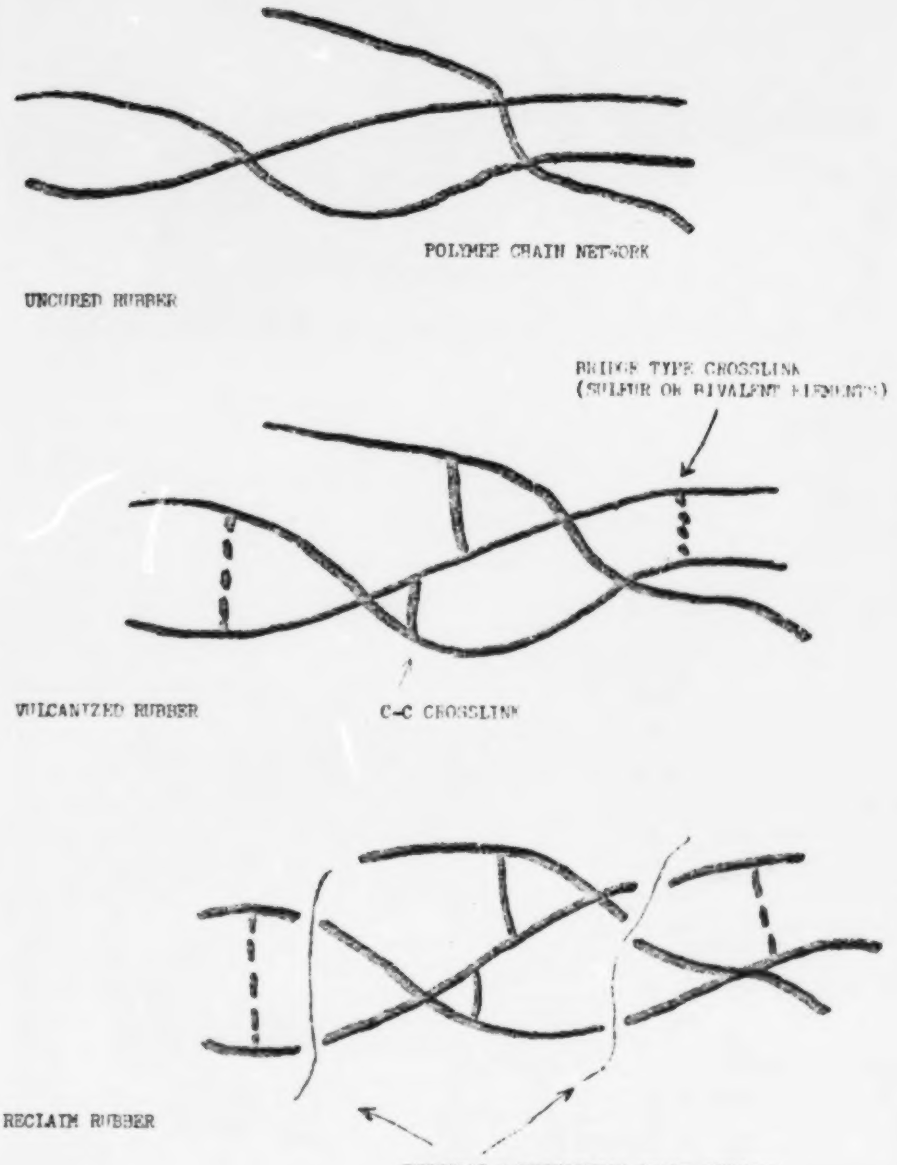

POLYMER CHAIN NETWORK
UNCURED RUBBER
BRIDGE TYPE CROSSLINK
(SULFUR OR BIVALENT ELEMENTS)
VULCANIZED RUBBER
C-C CROSSLINK
RECLAIM RUBBER
CHEMICAL & MECHANICAL CHAIN CISSION

Figure 9. Chemical mechanism of vulcanization and devulcanization.

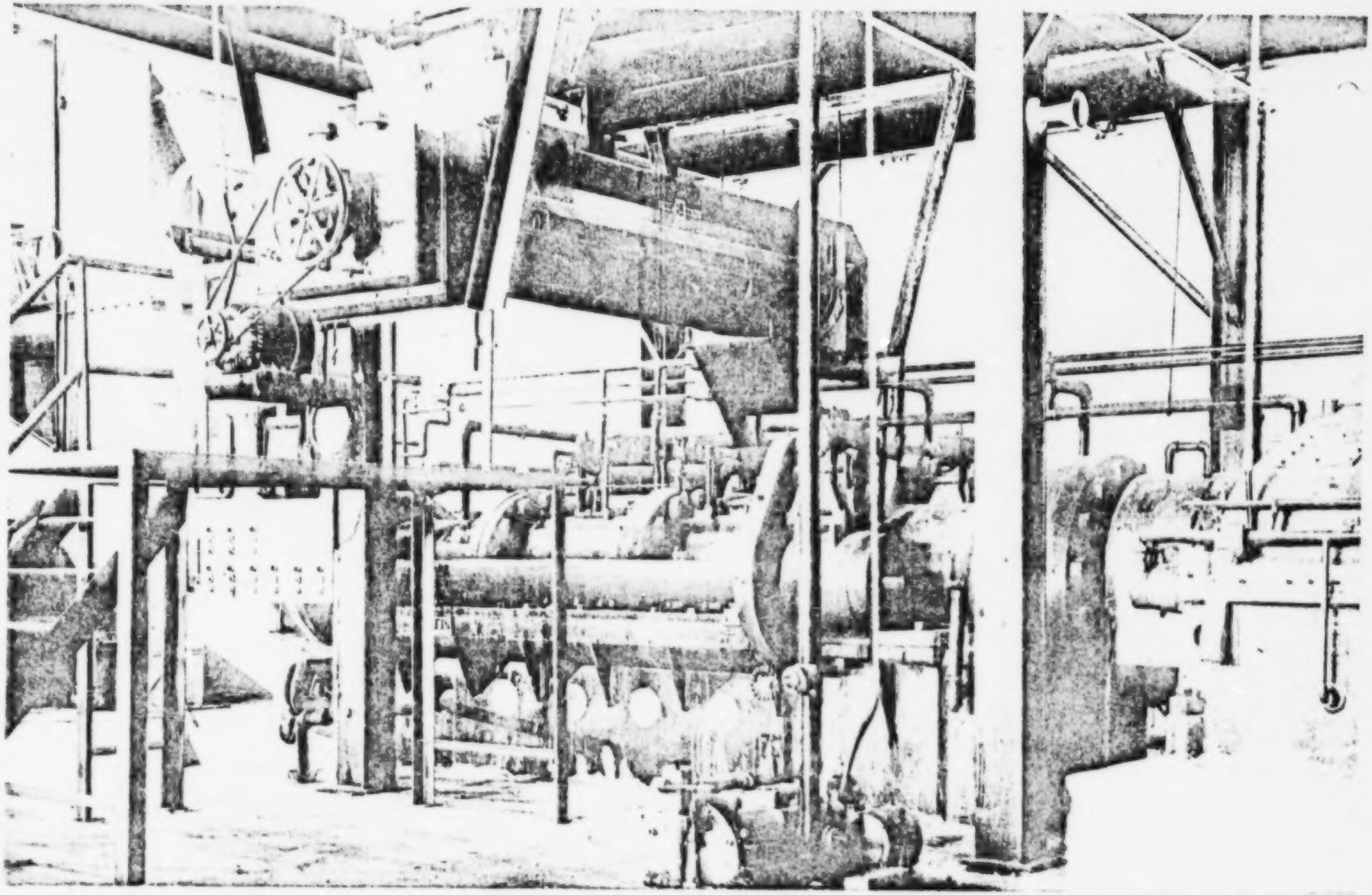


Figure 10. Reclaimator.

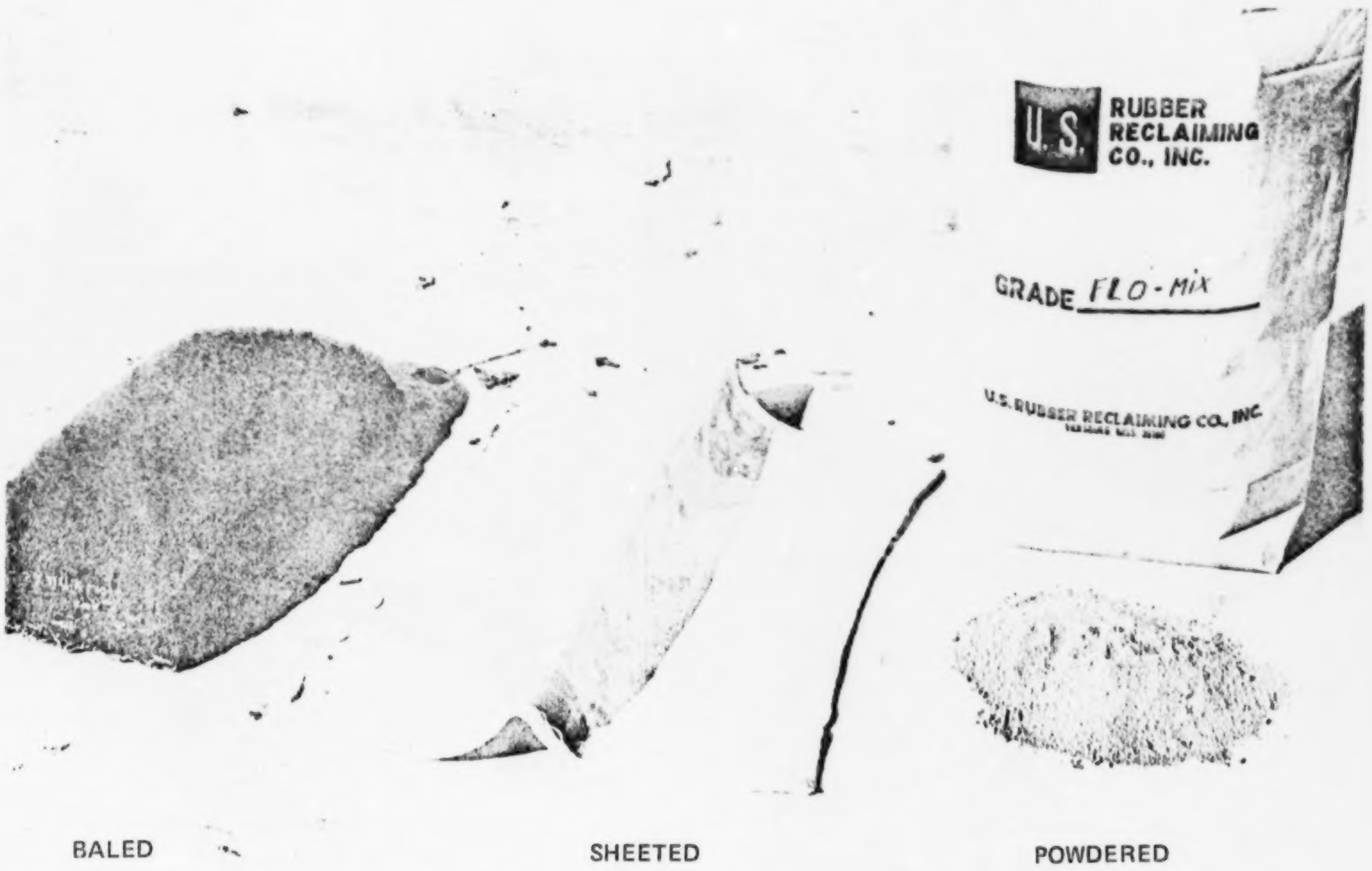

U.S.
RUBBER
RECLAIMING
CO., INC.
GRADE FLO-MIX
U.S. RUBBER RECLAIMING CO., INC.
BALED
SHEETED
POWDERED

Figure 11. Forms of reclaimed rubber.

FIELD PREPARATION OF RECLAIM RUBBERIZED JOINT SEALERS

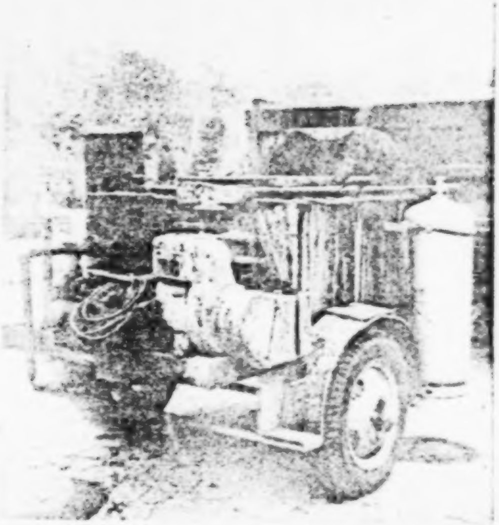


Figure 12. Asphalt kettle.

Figure 13. Addition of rubber to hot asphalt.

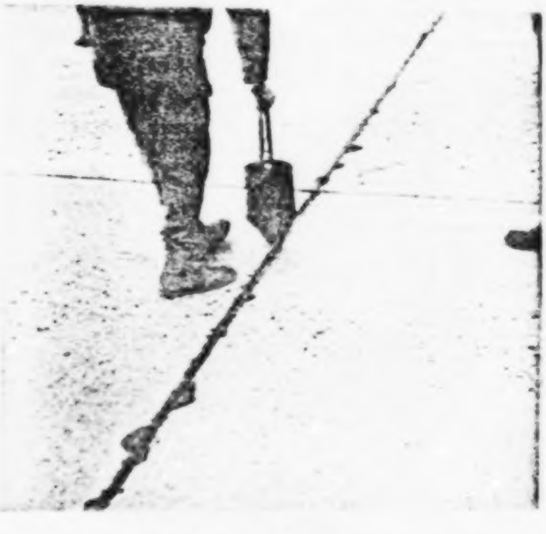


Figure 14. Pouring of rubberized joint sealer.

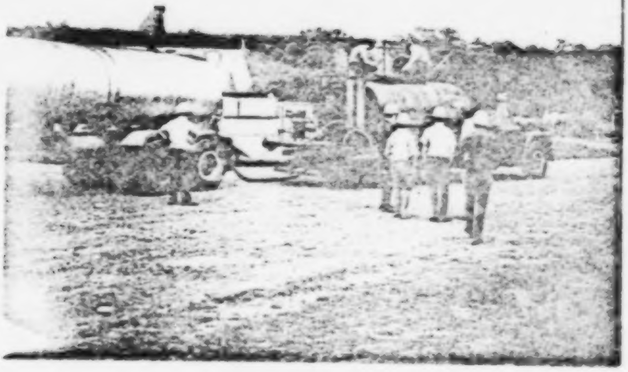


Figure 15. Transfer of asphalt to distributor.

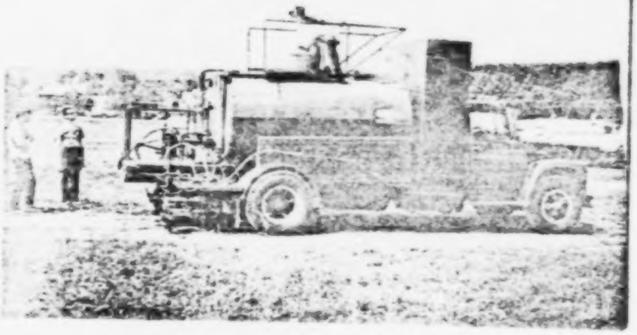


Figure 16. Addition of rubber to asphalt.

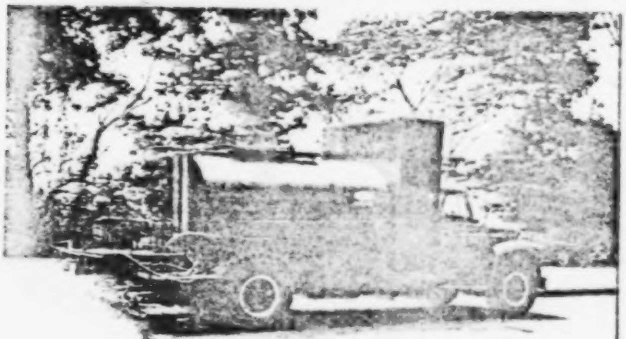


Figure 17. Spraying rubberized asphalt.

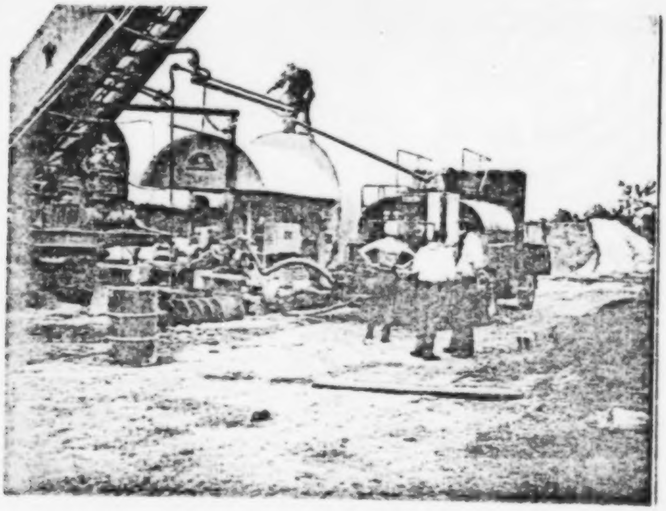


Figure 18. Connections required for using reclaim rubberized asphalt in hot mix asphalt concrete.

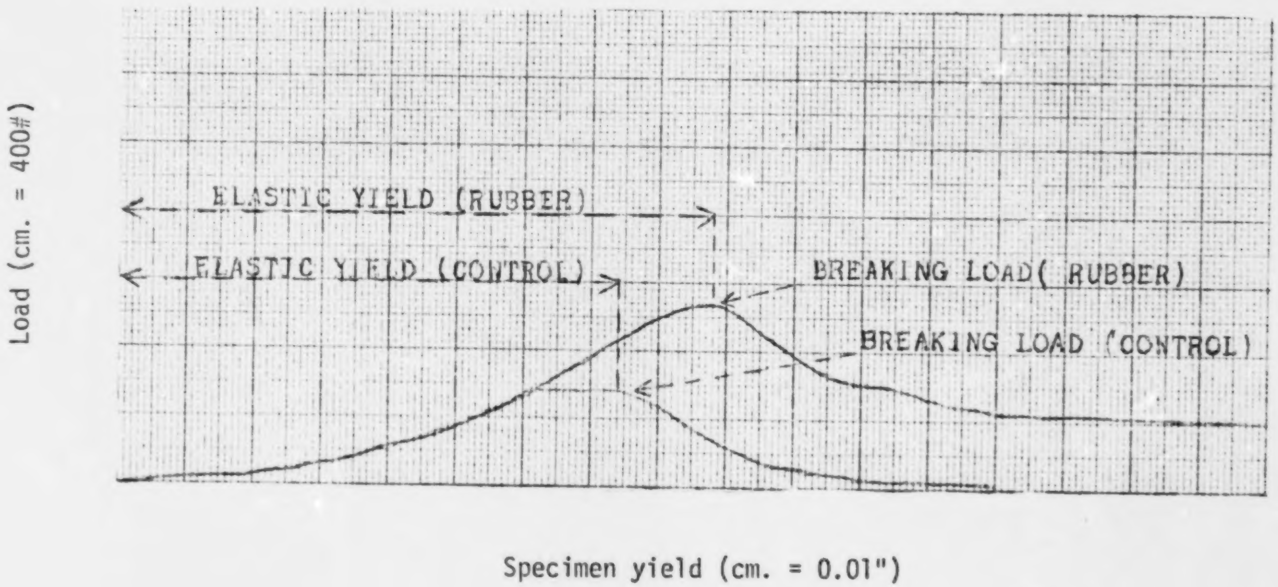
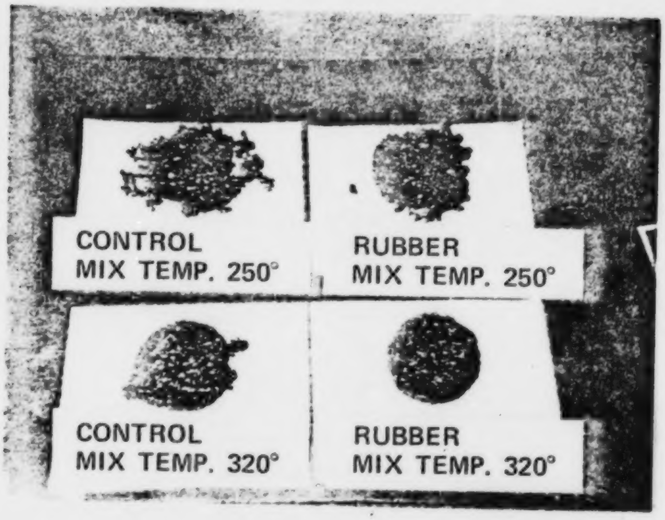
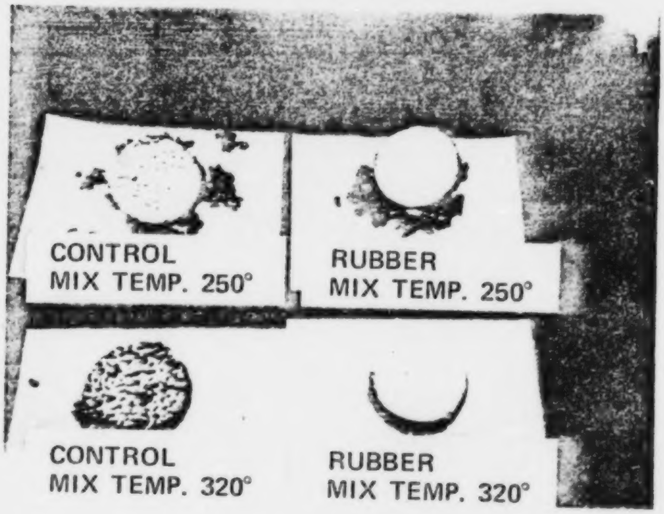


Figure 19. Split cylinder tensile tests of plant mix seal specimens @ 0°F.



CONTROL
MIX TEMP. 250°
RUBBER
MIX TEMP. 250°
CONTROL
MIX TEMP. 320°
RUBBER
MIX TEMP. 320°

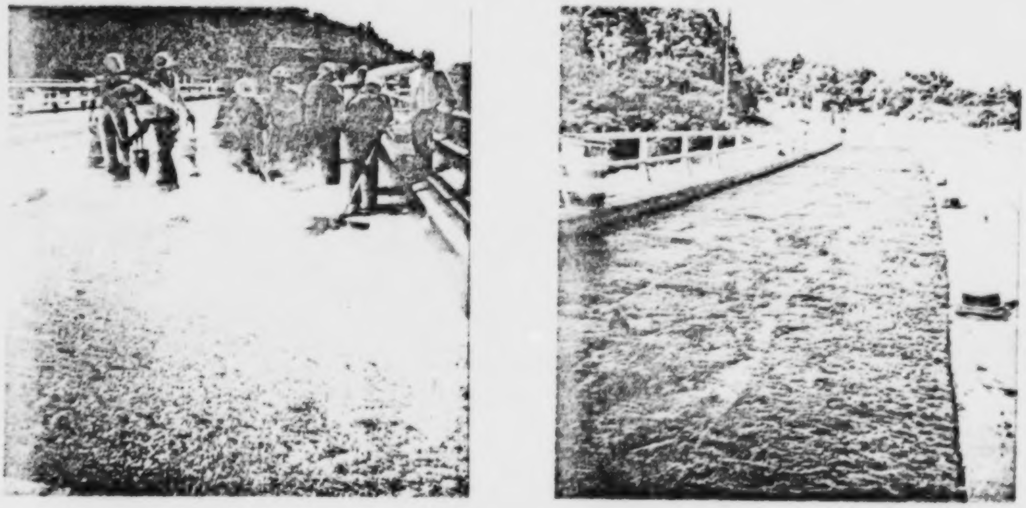
a. Cohesive properties of reclaim rubberized asphalt in plant mix seals at room temperature.



CONTROL
MIX TEMP. 250°
RUBBER
MIX TEMP. 250°
CONTROL
MIX TEMP. 320°
RUBBER
MIX TEMP. 320°

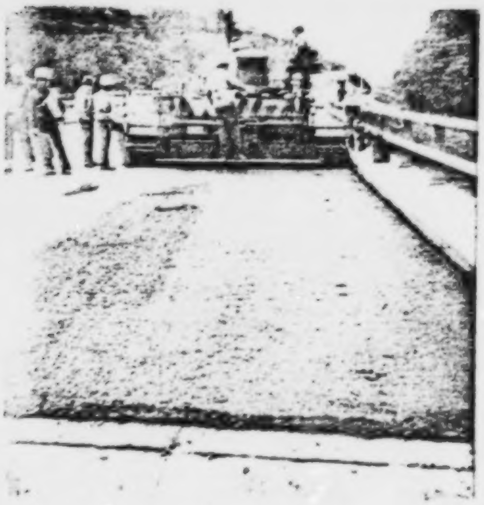
b. Drainage characteristics of reclaim rubberized asphalt in plant mix seals.

Figure 20.



a. Membrane placement.

b. Completed membrane.



c. Overlaying membrane.

Figure 21. Reclaim rubberized asphalt in a bridge deck waterproofing membrane.

STRAIN-RELIEVING INTERLAYER PLACEMENT

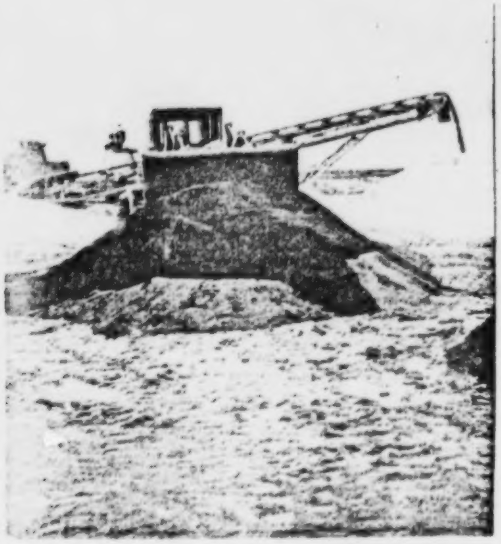


Figure 22. Preblending of rubber.

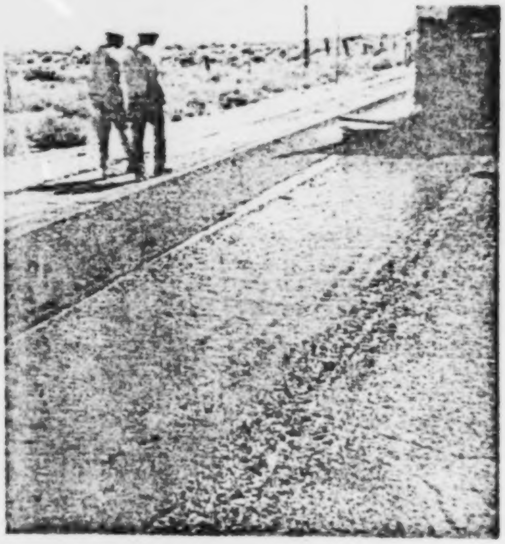


Figure 23. Placement of SRI slurry.

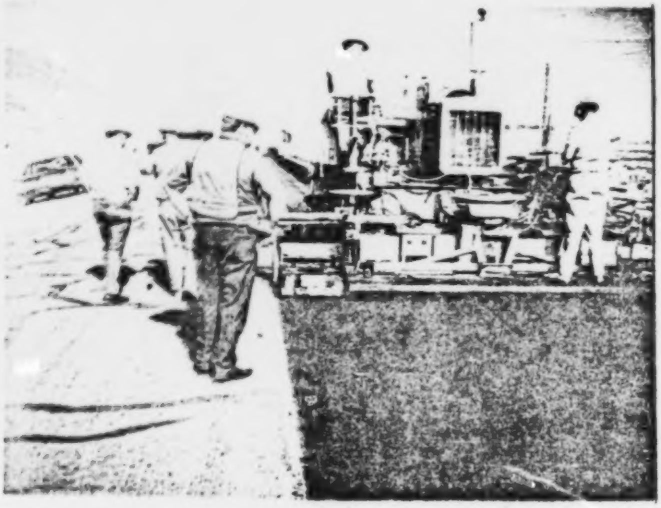


Figure 24. Overlaying of SRI slurry.

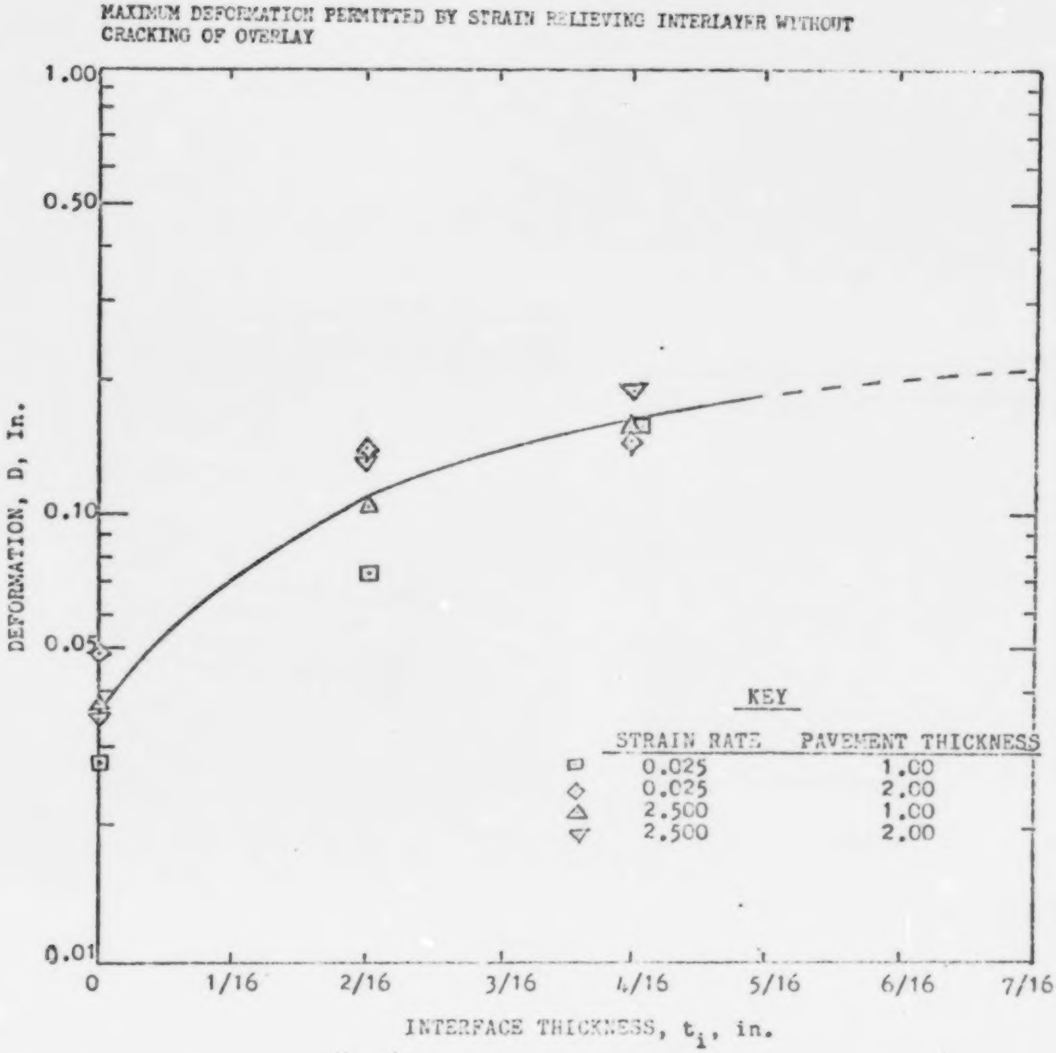
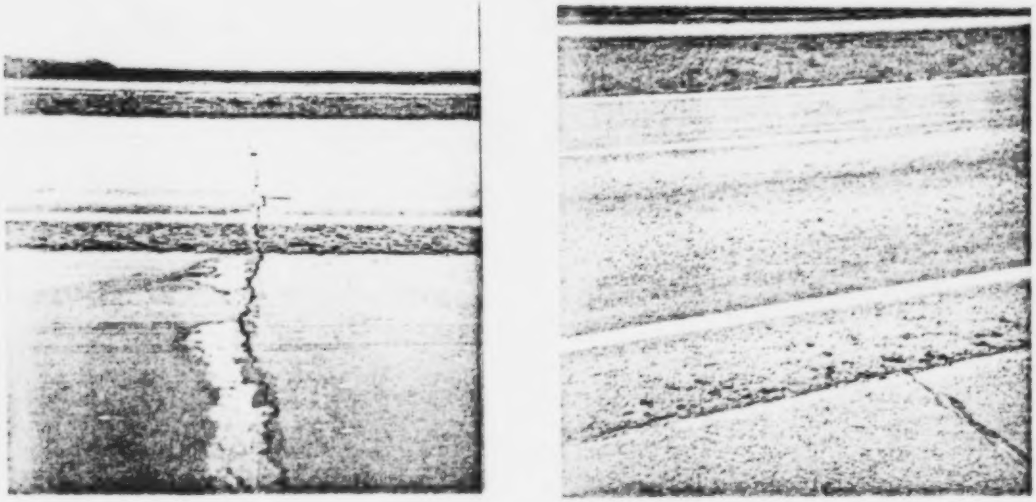


Figure 25. Analog deformation vs. interface thickness.



a. Control.

b. SRI

Figure 26. Strain-relieving interlayer test section after 3 years.

ENVIRONMENTAL ASPECTS OF RUBBER RECLAIMING AND RECYCLING (MANUFACTURING)

Robert C. Reinhardt*

Abstract

The reclaiming and recycling of rubber can appreciably help to conserve our natural resources and help eliminate scrap-tire disposal problems. This can be accomplished without any detrimental effect to our environment. This was not always the case.

Recently the pollution problems resulting from the reclaiming of rubber have been substantially reduced. This has been accomplished at considerable cost to the reclaiming companies remaining in business. A large number of reclaim plants have closed their operations rather than make expenditures required to meet today's stringent EPA air and water quality standards.

The reclaim plants still in operation have not only installed pollution control equipment, but have also developed new processes and new equipment that have materially reduced air and water pollution problems. The basic operations employed in the reclaiming of rubber, such as cracking (size reduction); defibering; devulcanizing (or depolymerizing); and refining needed to be individually monitored and tested. Operations in which today's pollution standards could not be economically met were shut down, and new or modified processes and equipment were developed and installed to produce the necessary functions.

Current processes will be continually modified to keep abreast of new air and water pollution requirements.

The following is a brief description of the various processing operations in a typical rubber reclaiming plant. Details of modern reclaiming methods, processing equipment, and pollution control equipment will be described and compared to previous ones.

The primary size-reduction systems now being used in the rubber

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*Manager, Project Engineering, Midwest Rubber Reclaiming Company, 3101 Mississippi Avenue, Sauget, Illinois 62202.

reclaiming operation have not changed appreciably in the last few years. U.S. and foreign manufacturers have introduced various new types of size reduction equipment that reduce the whole tire including the bead wire into pieces anywhere from 8- to 10-inch strips down to 3/4-inch particles. Some of this equipment employs a rotating cutter to obtain a rip, tear, or shear action, while others have rotating knife-type slitter actions. The capital cost for this equipment is much less than a standard corrugated two-roll cracker installation. This equipment cannot be successfully or economically used for reclaiming operations in which all the fiber, bead wire, metal, etc., must be removed.

RUBBER RECLAIMING (SIZE REDUCTION)
BEADWIRE AND METAL REMOVAL

Modern reclaiming plants (fig. 1), in order to keep material handling costs at a minimum, use either a belt or hook conveyor to feed the primary cracker or size-reduction equipment. Metal detection equipment automatically rejects steel-belted or studded tires before they reach the cracker. The bead wire that has been stripped from the tire carcass is manually removed after the first pass through the cracker. Gyratory-type classifier screens return the oversized particles to the cracker for further size reductions. The undersized material, after passing over magnetic separation equipment, can be directly conveyed to the secondary cracking operation or stored in a surge silo. Aspirators are employed at the secondary cracker and at the classifier screens to collect airborn tire fibers and dust particles as they are being produced. High-pressure pneumatic conveyors, in conjunction with high-efficiency cyclones or bag-type bin-vent collectors, are used to transfer the ground stock. The recycling belt conveyors are equipped with efficient magnetic removal equipment to collect any bead wire or ferrous metal before it is carried any further into the process. The combined rubber and fiber is ground to approximately 1/4- to 3/8-inch in size in the secondary cracking operation.

FIBER SEPARATION (COMBINATION OF AIR AND GRAVITY)

The feed rate of the ground stock (fig. 2) from the secondary cracking

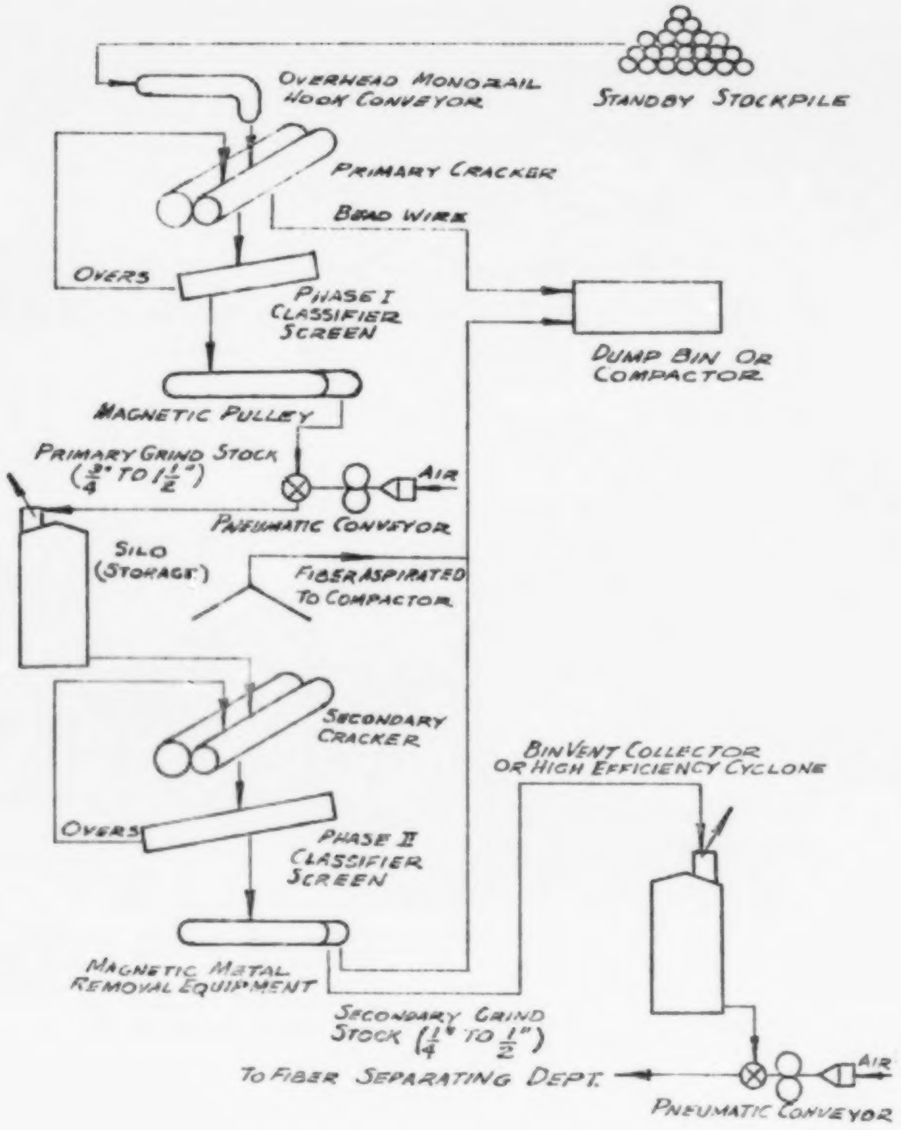
OVERHEAD MONORAIL HOOK CONVEYOR
STANDBY STOCKPILE
PRIMARY CRACKER
BEAD WIRE
OVERS
PHASE I CLASSIFIER SCREEN
DUMP BIN OR COMPACTOR
MAGNETIC PULLEY
PRIMARY GRIND STOCK (3/4" TO 1 1/2")
AIR
PNEUMATIC CONVEYOR
SILO (STORAGE)
FIBER ASPIRATED TO COMPACTOR
SECONDARY CRACKER
BIN VENT COLLECTOR OR HIGH EFFICIENCY CYCLONE
OVERS
PHASE II CLASSIFIER SCREEN
MAGNETIC METAL REMOVAL EQUIPMENT
SECONDARY GRIND STOCK (1/4" TO 1/2")
TO FIBER SEPARATING DEPT.
AIR
PNEUMATIC CONVEYOR

Figure 1. Flow diagram of rubber reclaiming (size reduction) beadwire and metal removal.

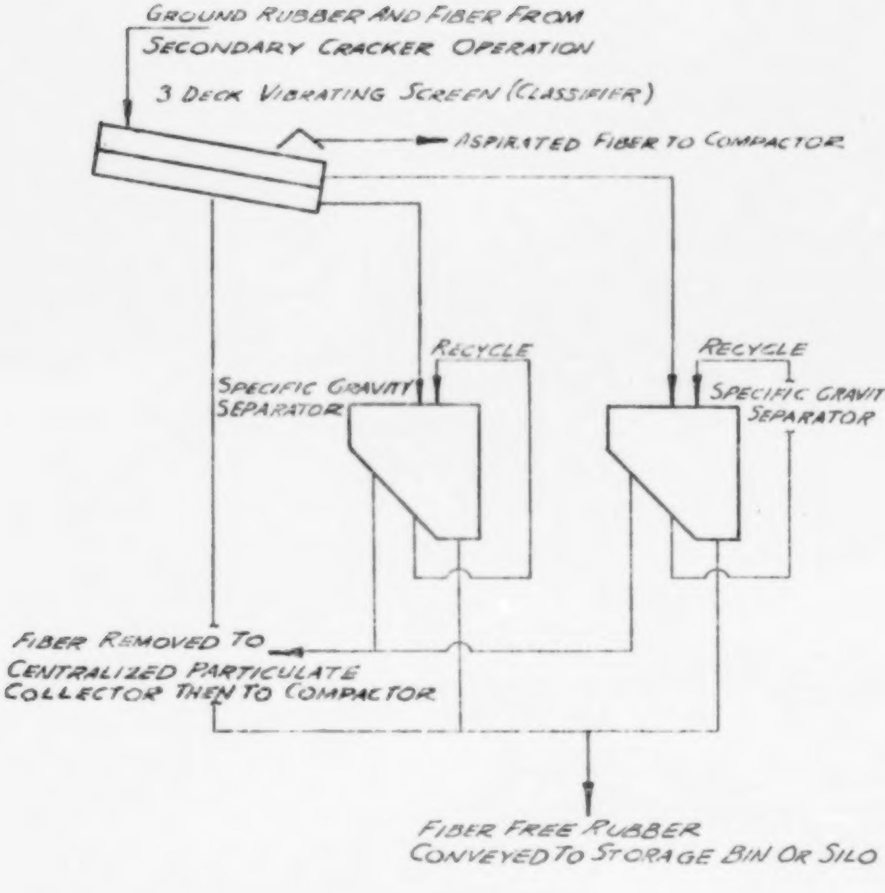
GROUND RUBBER AND FIBER FROM SECONDARY CRACKER OPERATION
3 DECK VIBRATING SCREEN (CLASSIFIER)
ASPIRATED FIBER TO COMPACTOR
RECYCLE
SPECIFIC GRAVITY SEPARATOR
RECYCLE
SPECIFIC GRAVITY SEPARATOR
FIBER REMOVED TO CENTRALIZED PARTICULATE COLLECTOR THEN TO COMPACTOR
FIBER FREE RUBBER CONVEYED TO STORAGE BIN OR SILO

Figure 2. Flow diagram of fiber separation (combination of air and gravity).

operation is controlled at a constant rate to facilitate the balancing of the specific gravity fiber-separating equipment. A primary classifying screen divides the product into four different product streams. The large fluffy fiber particles are removed at the top screen, conveyed directly to a centralized fiber collection system, and funneled into a high-density compactor. The second and third cuts from the classifying screen are screw-conveyed to fluidized-bed specific gravity tables. The "fines," passing through the classifying screens, along with the fiber-free rubber from the specific gravity tables, are vacuum conveyed to a pulse-air type bag collector, which utilizes a positive pressure air blower to develop the required vacuum. The fiber removed by the specific gravity tables is vacuum conveyed to the centralized fiber compactor system.

FINE-GRIND AND FIBER ASPIRATING EQUIPMENT

The fine-grind operation (fig. 3) reduces the 1/4- to 3/8-inch mostly fiber-free material to a size of approximately 20-30 mesh. Fine corrugated high-friction mills are employed in this operation. Classifying screens developed for removing husks from peanuts were modified and are employed to aspirate any additional fiber released during the fine-grind process. This fiber is also pneumatically conveyed to the centralized compactor system. The resultant fiber-free rubber is conveyed and stored in large silos to enable economic utilization of high-capital-cost, batch-type devulcanization equipment. The older low-efficiency, low-pressure conveying systems had to be replaced with positive-pressure pneumatic conveyors. Noise snubbers and high-efficiency collectors are now used in conjunction with this equipment.

The outmoded wet-digestor process for devulcanization (or depolymerizing) of cured rubber has been discontinued by most rubber reclaimers. Major problems in the areas of water and air pollution could not be economically controlled. The old wet-digestor process employed vertical jacketed autoclaves with a series of paddles mounted on a low-speed vertical shaft. Fairly large amounts of metal chlorides or sodium hydroxide and water were added to the scrap rubber to obtain uniform devulcanization and hydrolyzation of the fiber. This devulcanization process took anywhere

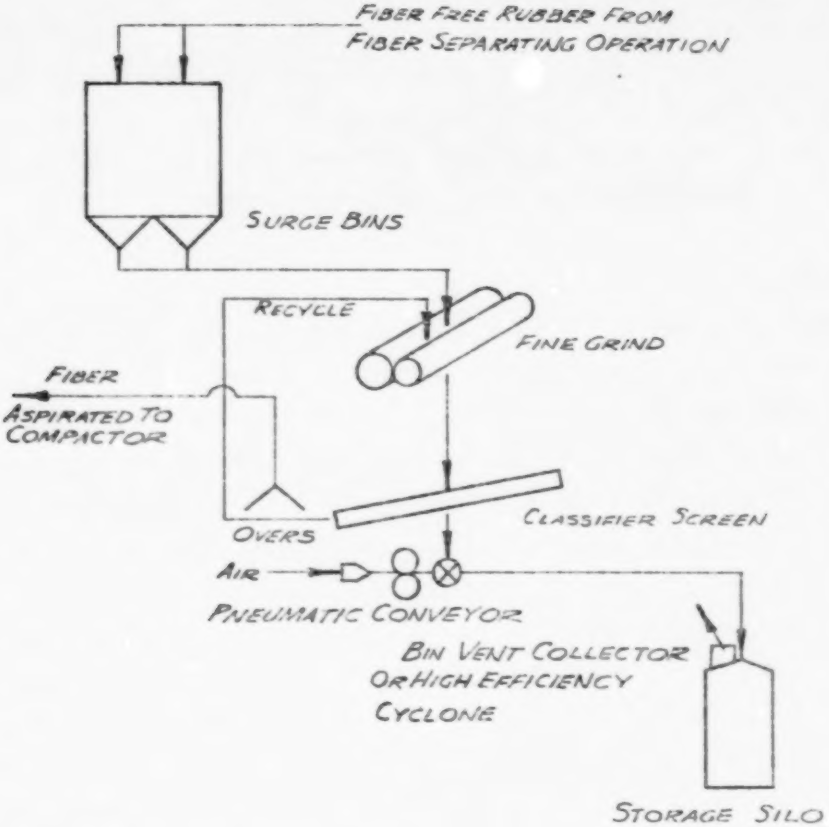
FIBER FREE RUBBER FROM
FIBER SEPARATING OPERATION
SURGE BINS
RECYCLE
FINE GRIND
FIBER
ASPIRATED TO
COMPACTOR
OVERS
CLASSIFIER SCREEN
AIR
PNEUMATIC CONVEYOR
BIN VENT COLLECTOR
OR HIGH EFFICIENCY
CYCLONE
STORAGE SILO

Figure 3. Flow diagram of fine grind and fiber-aspirating equipment.

from 8 to 12 hours to complete. A considerable volume of water was then required to remove the hydrolyzed fiber and chemicals adhering to the rubber. Additional water pollution problems were generated during the dewatering operation. The large air volumes required by the direct-contact type air-circulating dryers would have made particulates and odor emissions very costly to control.

DYNAMIC DEVULCANIZATION PROCESS

The dynamic devulcanizer (fig. 4) was developed to obtain a more uniform product and also to eliminate the disadvantages of major air and water pollution problems associated with the wet-digestor process. The devulcanizer vessel was designed to be operated at steam pressures up to 500 pounds per square inch, and also to facilitate rapid loading and unloading of the stock. This has resulted in much higher production rates than those obtained with a comparably sized wet digestor. Spiral-ribbon type agitators keep the product moving throughout the devulcanizer cycle, thereby resulting in extremely uniform depolymerization of the stock. Thus the major disadvantages of the dry pan or heater process, layering and nonuniform devulcanization of the cured rubber, are eliminated.

The blowdown of the dynamic devulcanizer is controlled at a constant rate to permit the use of a high-energy type Venturi scrubber. The effluent gasses from the dynamic devulcanizer enter the Vena Contracta, which is a restriction that accelerates the gas stream to a very high velocity. A scrubbing liquid is injected into the Vena Contracta by means of a spray nozzle and is atomized into fine droplets. Aerosol collection and gas absorption take place on the liquid droplets, which act as collection bodies, by inertial impaction and diffusion. The four major benefits obtained with the Venturi scrubber are as follows:

1. It collects fine particulate matter present in the gas stream;
2. It cools the hot dynamic devulcanizer discharge gasses and absorbs the water-soluble gasses;
3. It condenses oil and condensable malodorous gasses;
4. The eductor type Venturi pulls a vacuum on the devulcanizer vessel and thereby reduces the blowdown time to a minimum.

A barometric absorption scrubber is installed downstream of the

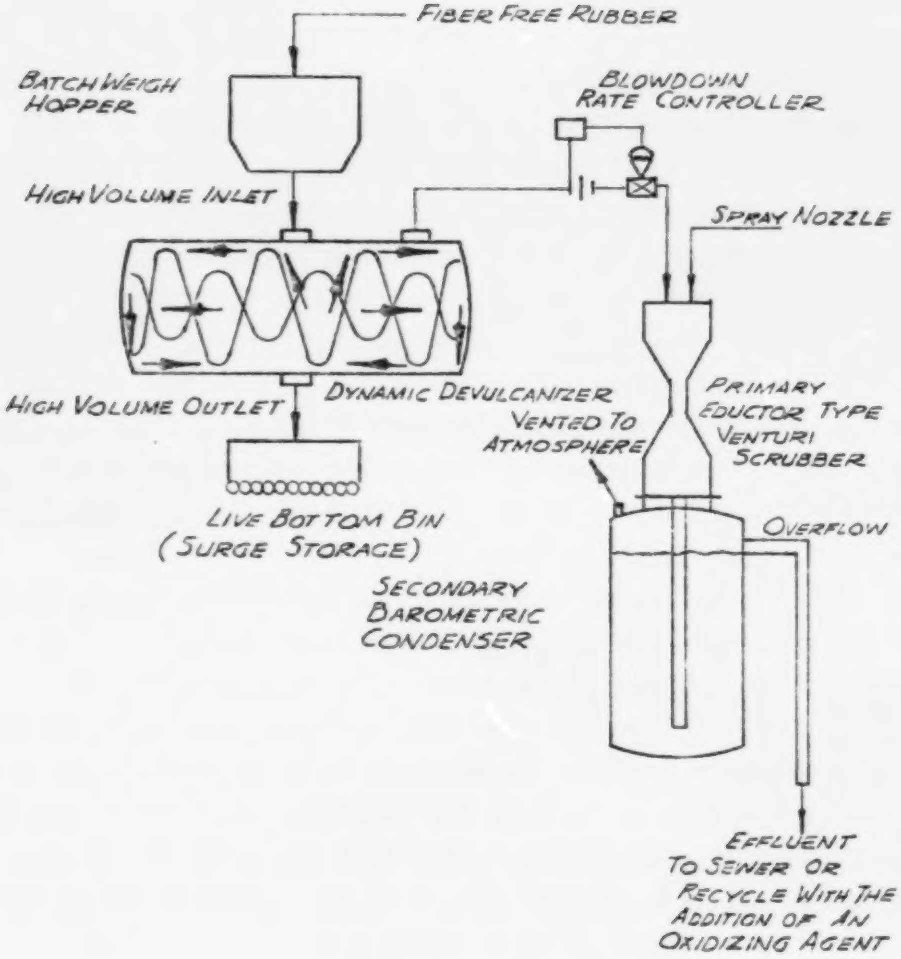
FIBER FREE RUBBER
BATCH WEIGH HOPPER
BLOWDOWN RATE CONTROLLER
HIGH VOLUME INLET
SPRAY NOZZLE
HIGH VOLUME OUTLET
DYNAMIC DEVULCANIZER
PRIMARY EDUCTOR TYPE VENTURI SCRUBBER
VENTED TO ATMOSPHERE
LIVE BOTTOM BIN (SURGE STORAGE)
OVERFLOW
SECONDARY BAROMETRIC CONDENSER
EFFLUENT TO SEWER OR RECYCLE WITH THE ADDITION OF AN OXIDIZING AGENT

Figure 4. Flow diagram of dynamic devulcanization process.

Venturi scrubber to remove any additional minor pollutants. Low-energy types of absorption scrubbers, such as packed towers, plate towers, and flooded bed scrubbers, etc., would quickly plug up due to fine particulates entrained in the blowdown gasses. Direct flame combustion and catalytic oxidation control equipment require tremendous amounts of energy for operation and therefore would not be suitable for this application.

MILL ROOM

In the millroom operation (fig. 5), a heavy-duty screw type blender is used to mix and disperse pigments and other ingredients added at this stage. Conventional screw conveyors and vertical rotolifts feed the stock to extended barrel mixer strainers. The stock is warmed up and plasticated in this operation. The stock is then fed to preliminary high friction breaker mills. The rolls on these mills are smooth and are geared to turn at different speeds. Crowning of one of the rolls results in a uniform pressure on the stock between the two rolls. The stock is then fed to a finishing strainer, where metal and other foreign particles are removed. To further improve the product quality, an additional pass through a finishing refiner is required. The rolls on the finishing refiner are set to obtain a rubber sheet thickness of from .004 inch to .006 inch. The thin sheet of rubber is scraped off the roll with a stationary knife that extends across the full length of the roll.

Each mill requires from 30 to 40 gallons of water per minute to remove the large amounts of frictional heat generated by the milling action of the rubber. Additional cooling water is required in the straining and mixing operations. The cooling water is pumped to wet cooling towers by means of recirculating pumps for reuse. The blowdown water from the cooling tower along with process and sanitary waste water is kept separate from the cooling water, thus reducing sewer effluent to the extent that it can be economically controlled and treated.

In the past the finished sheet from the refiners was collected on a windup drum. When the thickness of the stock reaches approximately 3/4 inch, the windup drum was stopped and the rubber slab was manually cut off with a small hand-held knife and placed on a dusting table. The thin

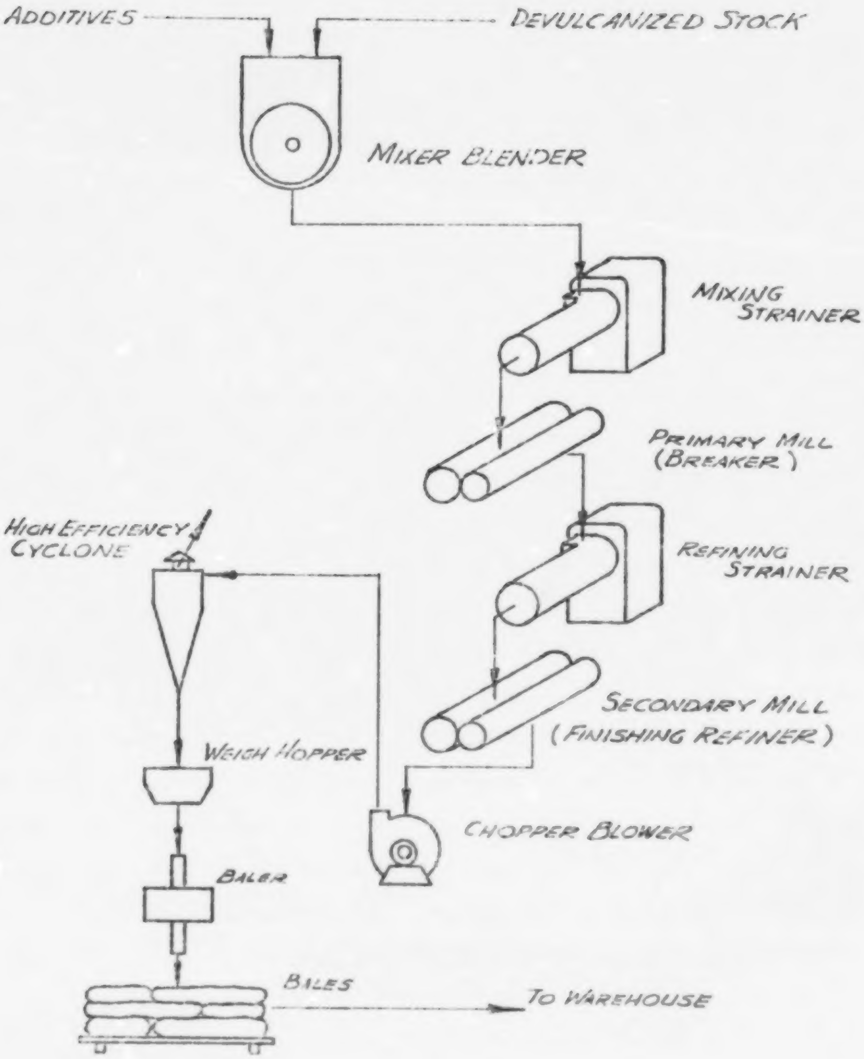
ADDITIVES
DEVULCANIZED STOCK
MIXER BLENDER
MIXING STRAINER
PRIMARY MILL (BREAKER)
HIGH EFFICIENCY CYCLONE
REFINING STRAINER
SECONDARY MILL (FINISHING REFINER)
WEIGH HOPPER
CHOPPER BLOWER
BALER
BALES
TO WAREHOUSE

Figure 5. Flow diagram of mill room.

sheet from the refiner had to be manually restarted on the windup drum. The rubber slab was then heavily dusted with talc and stacked for removal to the warehouse. The high dust concentrations in the vicinity of the operator were reduced somewhat with high-volume exhaust fans. High particulate amounts were thus emitted into the atmosphere.

A special heavy-duty combination chopper blower was developed to take the thin rubber sheet directly from the front roll of the finishing refiner. This sheet is carried by vacuum into the vortex of the blower, finely chopped, and then pneumatically conveyed to high-efficiency cyclones. The finely chopped product is automatically weighed before being loaded into an automatic high-density baler. The rubber is then compressed into 75-pound bales. The bales are stacked on skids and stored in the finished goods warehouse. This system eliminates the high amount of dust particles and the extensive amount of manual labor that is required in the previous operation.

I have covered the five basic operations in the reclaiming of rubber: primary size reduction, fiber separation, fine grinding, dynamic devulcanization, and milling and refining. I believe that the reclaiming and recycling of scrap tires will surely help to conserve our natural resources without any adverse effects on our environment.

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SHREDDED TIRES AS AN AUXILIARY FUEL

Robert H. Taggart, Jr.*

Abstract

A developmental study of the feasibility of burning a mixture of 10 percent shredded rubber and 90 percent coal by weight in an industrial-size stoker-fired boiler has been completed at General Motors Fisher Body Plant in Pontiac, Michigan. The equipment adapted for handling and mixing the shredded rubber with the coal has performed satisfactorily. There were no operational or deterioration problems with the boilers. Stack emission testing has shown compliance with both the Michigan State particulate and SO_2 *codes. Finally, at current prices, the rubber-coal fuel mixture represents a yearly savings of approximately 6 percent of the powerhouse fuel costs, not including capitalization costs on the rubber handling equipment. In addition, the intangible savings and benefits to the community on the critical disposal and energy problem being addressed by this system are difficult, if not impossible, to estimate.*

The problem of environmentally acceptable disposal of scrap tires is very complex with many options available for its solution. The low bulk density and noncompactibility of whole scrap tires plus their tendency to "float" to the surface of landfills discourage conventional landfilling as the disposal method. Their low biodegradability makes discarded tires a blight on the landscape for generations. Recycling, in the form of recapped tires, has decreased due to the availability of inexpensive new tires that can compete with recaps and due to more stringent safety standards on the tire carcass, which limit the number of used tires that meet the requirements for recapping. In addition, rubber reclamation has decreased due to decreased demand for secondary rubber products--e.g., carpeting is now used in autos rather than rubber mats. These factors all tend to increase the number of tires that must be disposed.

Many methods of scrap tire disposal and/or resource recovery are being

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*Project Engineer, General Motors Corporation, Environmental Activities Staff, Warren, Michigan 48090.

investigated to handle the approximately 250 million tires that are disposed of in the United States each year. Some of these methods are artificial reefs, filler for asphalt, concrete, etc., automotive crash barriers, energy recovery systems, and materials recovery systems.

General Motors' direct involvement in the concept of burning tires for fuel value and energy recovery began in 1970 when GM Manufacturing Development and Fisher Body-Pontiac carried out a 3-day experimental study in which they burned 30 tons of shredded tires in a 10-percent mix with 90-percent coal. This test was carried out at the Fisher Body-Pontiac Plant by mixing the shredded rubber directly with the coal through the coal car unloading grates. Air pollution emission testing indicated an increase in particulate emissions when the rubber and coal mixture was burned, but the emission levels were still within code. There were serious problems, however, with bridging of the rubber as it was fed through the coal car unloading grates. The low cost of coal, at that time, and the relatively high cost of shredding tires, plus the material handling problems associated with the shredded rubber, caused the project to be discontinued.

Due to the increasing problem of scrap tire disposal, the renewed interest in resource recovery and materials conservation and the increasing price of coal, members of the Environmental Activities Staff and Fisher Body-Pontiac reevaluated the project in 1973. The economics were favorable and the feasibility of solving the materials handling problem looked promising.

The powerhouse at Fisher Body-Pontiac has continuous-ash-discharge, traveling-grate, spreader-stoker-fired boilers. This type of equipment is particularly suitable for firing shredded rubber. The spreader stoker can handle a wide range of fuels, has a quick response to changing steam load demands, and introduces the fuels so that the fires can be burned in suspension and the larger material is burned on the grates. The continuous-ash-discharge traveling grates give high heat release per unit area, handle fuels with widely varying ash contents, allow maximum residence time of the fuel on the grates, and give a good fuel distribution.

Other industrial-size boilers that should be able to burn shredded rubber and other selected waste materials successfully include the chain grate, traveling grate, vibratory grate, and underfeed stoker. Newly designed pulverized coal-fired boilers with the capability of burning solid waste above the tangentially-fired pulverized coal and having bottom grates for complete burnout may also be able to burn shredded rubber.

A system was adapted to handle the shredded rubber, as shown in figure 1. As the system was operated during the study, a front-end loader dumped the rubber onto a small conveyor, which transported it to the air-lock hopper rotary feeder. The rubber was then transported pneumatically from the feeder to the glass-lined 14-foot diameter and 40-foot-high silo for storage. A rotary chain unloader at the bottom of the silo was used to deliver the rubber on top of the coal as it traveled up the main conveyor to the coal bunkers. From here on, the mixed fuel was handled as in a conventional coal handling system.

Improvements in the rubber handling system for routine operation are now being considered. Instead of using a pneumatic system, Fisher Body is investigating a live bottom bin into which the truck delivering the shredded rubber could dump directly. The rubber would then be transported to the silo using a bucket elevator. This system change would decrease manpower requirements and the associated costs and also simplify system operations. Other potential benefits would be elimination of any dust problems related to pneumatic transport of fine materials and compaction problems in the silo caused by a pressurized system.

Another improvement could be made by increasing the horsepower on the chain unloader at the bottom of the silo, which would help in unloading the rubber onto the coal conveyor.

Before discussing the results of the study, some comment on the characteristics of rubber as a fuel should be mentioned. These are shown in table 1.

The rubber burned at Fisher Body is purchased from a tire recapping firm. This firm collects tires, recaps those suitable for recapping, and shreds the balance for use as asphalt pavement topping, garden mulch and fuel. The rubber must be shredded to be suitable for fuel, and the current supplier uses the Farrel Cracker Mill. Cut rubber from another source,

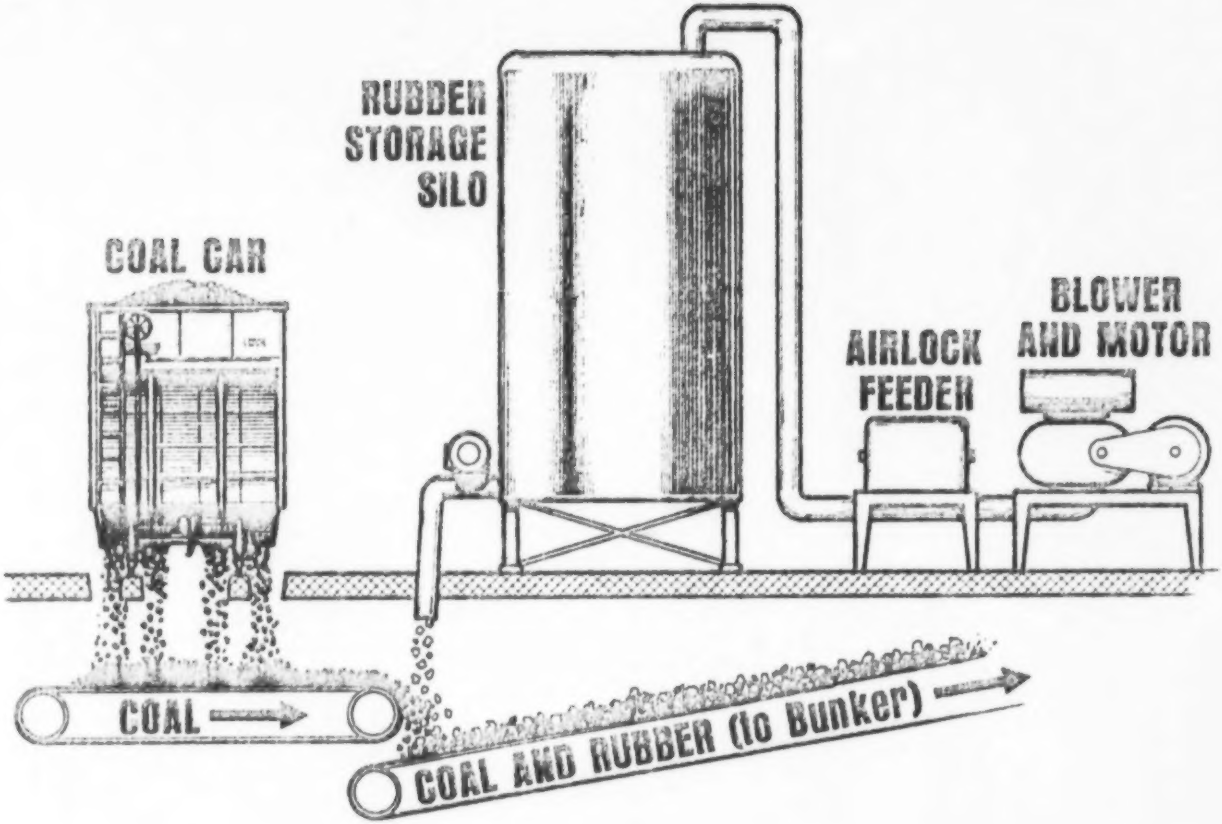
RUBBER
STORAGE
SILO
COAL CAR
AIRLOCK
FEEDER
BLOWER
AND MOTOR
COAL
COAL AND RUBBER (to Bunker)

Figure 1. Rubber handling system.

using a smaller commercially available machine, jammed the stokers due to the heavy cross section from the shoulder of the tire.

Assuming the following:

Cost of coal:	$40 per ton delivered
Cost of shredded rubber:	$24 per ton delivered
Heating value of coal:	12,500 Btu per pound
Heating value of shredded rubber:	15,000 Btu per pound
Mixture ratio (by weight):	10 percent rubber to 90 percent coal

there is an approximate 6-percent savings in overall fuel costs by burning the mixed fuel. This figure does not allow for depreciation of the capital equipment that had to be installed to handle the rubber in this case. It also does not reflect fluctuations in fuel costs.

A total of five particulate emissions tests were carried out on various boilers burning the 10-percent to 90-percent coal mixture. The percent increase in particulate emissions for each test burning the rubber and coal

Table 1. Characteristics of rubber

A. Btu Content
    1. Pure rubber - approximately 18,000 Btu/lb.
    2. Shredded rubber tires - approximately 15,000 Btu/lb.

B. Trace Element Concentrations
    1. Sulfur - approximately 1 percent..
    2. Zinc oxide - approximately 2 percent.

C. Materials Handling Characteristics
    1. Shredded rubber has a tendency to bridge.
    2. Stringers from reinforcing material can tie up rotating equipment.
    3. Rubber chips had a tendency to compress and become caught in the stokers.
    4. The size and purity of the shredded rubber was critical to materials handling throughout the system.
        a. The nominal size required was 1" × 1" × 1/4".
        b. The shredded rubber must be substantially free of metals--bead, belting, etc.

Table 2. Percent increase in particulate emissions for tests burning rubber and coal mixture over simple coal-firing

Test name	Percent particulate increase
MD #1	37
MD #2	65
Vendor #1	63
Vendor #2	75
Vendor #3	72

mixture over simple coal-firing is shown in table 2.

The average particulate increase over coal-firing is 62.4 percent. Of this 62.4-percent increase, 15.0 percent is zinc oxide. The remaining 47.4-percent increase in particulate emission is assumed to be composed of tire belting material, other structural material in the tires, and grinding fines.

The increase in particulate emissions when shredded rubber was burned caused a slight increase in plume opacity.

An area of specific concern, related to burning rubber from scrap tires, is in the area of increased zinc oxide particulate emissions. The vendor's test results indicate an increase in zinc oxide emissions from 0.09 pounds per hour when burning coal alone to 10.2 pounds per hour when burning an approximate 10 percent rubber to 90 percent coal mixture. In order to assess the impact of these increased emissions, a computerized diffusion model study was done on the Fisher Body-Pontiac powerhouse.

The first phase of the computer modeling study was to determine the maximum 8-hour ground-level concentration of zinc oxide under the worst meteorological conditions and worst emissions case. A search of the Pontiac Airport meteorological records for 1971 indicated the worst conditions to be a winter day with a 13.5-knot wind (approximately 15 miles per hour) and "D" stability. Since the wind direction and velocity did not change significantly during the 8-hour period, the computer model, which gives 1-hour predictions, could be applied to this particular 8-hour case. It was also assumed that the powerhouse was operating at near peak capacity (using 1973 peak load data) for the full 8-hour period. This assumption will overestimate emissions.

Figure 2 shows the results of this "worst case" computer modeling study. It indicates a maximum ground-level concentration for 8 hours of 42 $\mu g/m^3$ at a distance of 1,000 to 1,100 meters. This level is far below the 8-hour concentration of 5,000 $\mu g/m^3$ established by the American Conference of Governmental Industrial Hygienists in 1974.

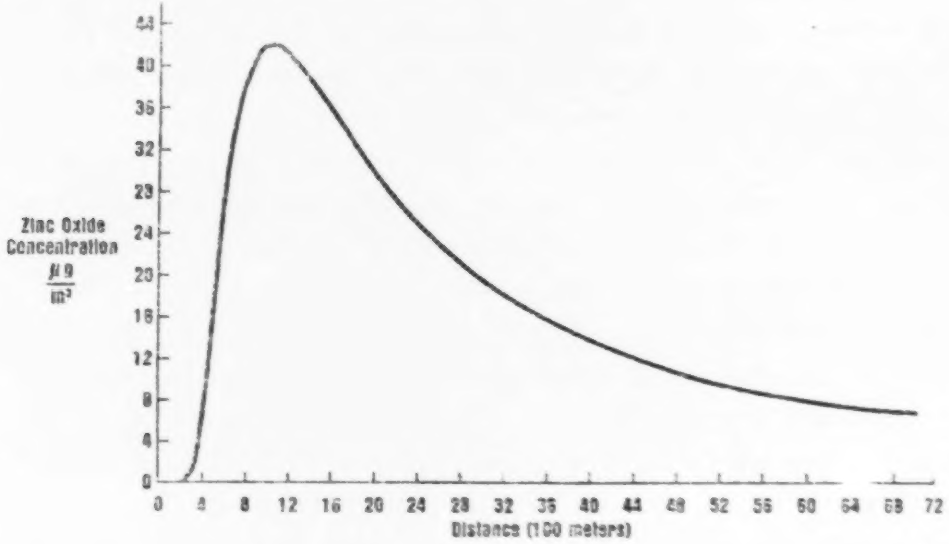

Figure 2.

The second phase of the computer modeling study dealt with obtaining maximum annual average ground level concentrations at specific locations. The AQDM (Air Quality Display Model), using the Briggs 69 plume rise equation, was used to obtain seasonal maximum average concentrations at various receptor locations.

The receptor locations having the highest annual average concentration were numbers 99 and 84. Number 99 had an annual average zinc oxide concentration of 0.3950 $\mu g/m^3$, and number 84 had an annual average zinc oxide concentration of 0.3756 $\mu g/m^3$. These are both well below the 50 $\mu g/m^3$ annual average contained in an EPA report entitled "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste."* These comparisons indicate that the system at Fisher Body-Pontiac poses no health hazards from increased zinc oxide emissions.

As indicated by the vendor's tests (table 3), sulfur dioxide emissions actually decreased as a result of burning the mixed fuel. The rubber, which has a low sulfur content (approximately 1 percent) and a high Btu per pound, decreases the SO_2 generated per Btu of heat release.

The operations of the boilers have been monitored throughout the approximately 6 months that the coal-rubber mixture has been burned. The powerhouse chief and boiler operators report that there are no adverse effects to any powerhouse equipment when the coal-rubber mixture is burned. Operation of the boiler itself was not affected. The only problems encountered were when the metal bead was not removed from the shredded rubber or the rubber was not shredded to a small enough size. In both cases, the feeders would jam and/or not operate properly.

Periodic examination of the boilers and tubes after firing the coal-rubber mixture indicated no increased rate of boiler deterioration or any other related materials problems.

A final mention should be made concerning odor problems associated with burning rubber tires. Due to the high temperatures and high excess air** used in industrial stoker-fired boilers, there were no odor problems

Table 3. Sulfur dioxide emissions
(ppm)

Test name	Coal	Coal and rubber
Vendor Test #1	Bad Test	489
Vendor Test #2	627	433
Vendor Test #3	552	503

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*TRW Systems Group, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste," Vol. 1, EPA-670/2-73-053a, August 1973, p. 201.

**Excess air is that amount of combustion air in excess of that required for perfect stoichiometric combustion of a fuel in a boiler. It is a common expression among powerhouse and fuel people.

encountered in burning the shredded scrap rubber.

Overall, there seems to be an environmental tradeoff inherent in this system. Burning a mixture of coal and rubber in industrial stoker-fired boilers will increase particulate emissions from the boilers; however, unless very low-sulfur coal is being burned, the sulfur dioxide emissions will decrease. From a solid waste management standpoint, this system is extremely beneficial because it is an economically feasible method of utilizing a product that has been a major disposal problem. The potential energy savings from decreased coal use is also of major significance. Assuming all tires scrapped in a year were converted to energy, the Btu content would be equivalent to approximately 3.75×10^6 tons of coal or 6.94×10^8 gallons of oil.

There are several other aspects of this system which should be considered in the future. The rubber handling systems used in this study may not be applicable to all powerhouses. In fact, smaller powerhouses that use a front-end loader to feed the over-bunker conveyor may be able to mix the coal and rubber from two separate piles immediately before loading the coal conveyor and thus eliminate all of the capital equipment. It also may be possible to mix the coal and rubber as it arrives by truck, using a front-end loader and then simply handling the fuel mixture as pure coal has been handled previously. In order to assure safety in this method, the potential for spontaneous combustion in a mixed fuel pile should be evaluated.

Another area which should be explored further is the burning of cut rubber. Smaller and less energy-intensive machines are available for cutting rubber into small chips. The big problem is that these chips tend to jam and clog conventional stokers. Other mechanical or pneumatic stokers may be able to handle them, however. Besides saving energy in the rubber preparation step, the big advantage of burning rubber chips should be decreased particulate emissions. The much lower percentage of fines and the fact that the chips would burn on the bed rather than in suspensions should descrease particulate emissions.

An economic evaluation of the costs to upgrade the air pollution control devices so that higher concentrations of shredded rubber could be burned at selected sites should be done. The possibility of economic recovery of zinc from the particulates in the air pollution control device should also be considered. Along with this study, an evaluation of the effect of zinc on the operation of an electrostatic precipitator should be made.

Continuing evaluation of equipment deterioration caused by burning a mixed fuel of rubber and coal and all waste-burning systems should be made.

Since material handling still seems to be the major problem with the tire burning system and all waste burning systems, a continuing evaluation of these systems should be made.

THE TIRE-FIRED BOILER*

William L. Cox†

Abstract

Though scrap tires constitute less than 1 percent of the Nation's solid waste, they present a unique disposal problem since, without subdivision, they are unsuited for landfill operations.

One potential solution to this problem is the use of scrap tires as fuel. This application recovers approximately 40 percent of the thermal equivalents of all the fossil fuels consumed as raw materials and energy in the construction of the original tire.

The tire-fired boiler, installed by the Goodyear Tire & Rubber Company at its Jackson, Michigan, plant, employs the rotating hearth concept of Lucas American Recyclers. Such a unit requires a higher initial capital investment than do comparable oil- or coal-fired boilers, but affords appreciably lower total operating costs. In the case of fully depreciated units, tire-fired boilers burning scrap tires costing $20.00/ton are predicted to yield cost savings of from 34 to 56 percent when compared to those burning conventional fuels.

The tire-fired boiler thus meets the needs of American society today; it generates cheaper steam at no drain on fossil fuel sources while contributing a most viable solution to the disposition of a troublesome solid waste component.

New tires are produced at a rate of 150-200 million units per year, in a variety of sizes and constructions. Following their useful service life, normally from 1 to 10 years, more than 90 percent become a part of the Nation's solid waste. Though tires constitute slightly less than 1 percent of such waste, those properties that contributed so greatly to their utility--shape, strength, and nondegradability--become marked handicaps in their disposal. Without further subdivision they are poorly suited for landfill operations, and attempted disposition by burning in normal incineration results in the generation of heavy, acrid smoke so that such burning is generally prohibited.

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†Manager of Scientific Liaison, Goodyear Tire & Rubber Co., Akron, Ohio 44316. Paper was presented by Joe M. Smerglia, Corporate Environmental Engineer, Goodyear Tire and Rubber Company, Akron, Ohio.

These disposal problems and the difficulties they pose to communities in solid waste handling have been of major concern to the tire industry. Obviously, the best solutions to this ecological problem would be those involving the least disposal cost--and preferably ones which generate useful values from the disposal process. Consequently we have witnessed over the past several years industry-wide and individual corporate support for tire-based artificial reefs, floating breakwaters, erosion mats, highway impact barriers and such applications, which utilize the characteristics of scrap tires for maximum benefit. These solutions, unfortunately, tend to be limited with respect to geographical locations and to the number of tires that may be utilized in such applications.

The scrap tire, however, does have an additional property not mentioned above. It is composed chiefly of vulcanized rubber, and this rubber has a heat of combustion intermediate between those of coal and fuel oil. Under properly controlled combustion conditions it is an excellent heat energy source. Recognizing this, companies in various locations, both industrial manufacturers and utilities, have successfully experimented with the mixing of ground or cubed rubber with coal as a fuel for spreader-stoker boilers.

Incineration of scrap tires in this manner does suffer from the drawback of the energy, manpower, and equipment required to subdivide the scrap tire into a useful form. Goodyear believes it has another more satisfactory method of heat generation from whole tire combustion in the tire-fired boiler it elected to install at its Jackson, Michigan, tire plant.

This furnace, originally designed by Lucas American Recyclers, was chosen after an investigation of tire-fired boiler equipment suppliers by Goodyear's Corporate Engineering Department in 1971. The basic furnace design was developed by Lucas Furnace Development, Ltd., of England, with the engineering design and construction being rendered by Lucas American Recyclers and Fluor Utah. The design included a furnace with the design capability of burning 36 tons of scrap tires per day and a boiler to generate 25,000 pounds of steam at 250 psi per hour. Stack gas cleaning equipment was incorporated as a contingency to reduce particulate and SO_2 emissions (though tires contain less than 1 percent sulfur) to comply with possible air pollution standards.

The furnace operates continually without supplementary fuel at a temperature high enough to melt all the noncombustible material such as bead wire and fiber glass. It utilizes a rotary hearth that is sloped to a central ash discharge port. This hearth is refractory-lined and water-cooled around the center to protect its metallic body from the high temperatures developed inside the furnace.

Tires are fed onto the hearth from a vestibule by means of a pusher ram. Tires enter the vestibule through a door that closes as the furnace door opens to receive the tires. The hearth can revolve at rates of from 1/4 to 8-1/2 revolutions per hour with its rate set manually so that the tires are completely consumed in two revolutions (in normal burning, hearth rates are in the range of 2.7 to 6.0 revolutions per hour).

Initial tests of the unit in 1973 showed poor furnace performance as a result of hearth and air pattern problems. Correction of these problems and modification of unsatisfactory auxiliary equipment was made and the first tire burned in March 1974. Subsequent tests revealed that the furnace performed well at a burning rate of 4,400 lbs of tires/hr--40 percent over design. At this rate, using only water, not caustic, in the desulfurizer system, sulfur dioxide emissions were only one-third those permitted for solid fuel-fired boilers in Michigan.

At the design rate, particulate emissions were below the maximum allowable emission of 0.65 lb/1000 lb dry gas for coal-fired boilers generating less than 100,000 pounds of steam per hour.

During the initial furnace operations, analyses showed that the ash was extremely low in zinc, while particulate matter was suprisingly high in this element. We have concluded that at the extremely high temperatures generated and in the presence of the hydrocarbon components of the tire, zinc compounds are reduced to metallic zinc, distilled from the burning tire, and reoxidized by excess air to zinc oxide. By proper design of subsequent installations this zinc may be recovered and reprocessed to supplement virgin zinc ores, much of which must currently be imported.

The steam generated by the tire-fired boiler is a necessary part of the Jackson operation. If this boiler had not been installed, a similar one based on conventional fuels would have been required. Extensive test operations reveal that the boiler is functioning well, supplying the necessary steam with no appreciable consumption of fossil-based fuels, and reducing the number of discarded tires in solid waste by a million or more yearly. It is, moreover, recovering from those tires 40 percent of the thermal equivalent of all the crude oil, coal, and natural gas originally consumed in furnishing the material and energy for their manufacture.

The installation of the tire-fired boiler by Goodyear was conceived with the realization that the project would most probably involve excessive amounts of capital compared to a unit burning conventional fuels and would have an operating cost similar to conventional units. It was an attempt to pioneer a tire disposal approach, on a larger scale than had ever been attempted previously, as a contribution to solid waste problems. With the rapid and continuing rise in the costs of alternative fuels, the tire-fired boiler economics look better every day, as shown in table 1. Here operating costs of equivalently sized boilers fueled with scrap tires, oil, and low sulfur coal are compared. Capital costs for each case include the cost of the building to house the boiler. Other equipment included is listed below:

Fuel	Equipment
Tires	As previously described
Oil	200,000 gallon oil storage tank
Coal	Stoker, mechanical dust collector, coal handling conveyor, ash handling system, coal bunkers.

(Since a coal-fired boiler equipped with a sulfur removal system would cost more than a tire-fired boiler in order to burn high-sulfur coal costing ~ $26.00 per ton, its economics are obviously inferior to those of the tire-fired unit).

Table 1. Costs of steam generation
30,000 lb/hr, 250 psi

	Scrap tires		Oil		Coal	
Capital investment - $ M	1,500		320		800	
Btu value of fuel	13,000/lb		140,000/gal		12,000/lb	
Fuel requirement - daily	48 tons		8,900 gal	6,120 gal	52 tons	38.25 tons
- annual	16,800 tons		3,115,000 gal	2,142,000 gal	18,200 tons	13,400 tons
Unit fuel cost	$10.00/ton	$20.00/ton	$0.33/gal	$0.33/gal	$45.00/ton	$45.00/ton
Annual costs - $ M:						
Capital related						
Depreciation @ 4%	60	60	13	13	32	32
Interest @ 10%	150	150	32	32	80	80
Taxes, ins. @ 3%	45	45	10	10	24	24
Total	255	255	55	55	136	136
Operating costs						
Fuel	168	336	1,028	707	819	603
Labor & supervision	65	65	50	50	65	65
Maintenance	25	25	5	5	25	25
Utilities	10	10	8	8	10	10
Total	268	436	1,091	770	919	703
Total annual cost - $ M	523	691	1,146	825	1,055	839
Annual cost after full depreciation	313	481	1,101	780	943	727

In these calculations the oil and fuel requirements are assigned on the basis of (1) equivalent Btu content and (2) proven requirements for generating 30,000 lb/hr of steam at 250 psi.

The efficiencies of the conventional fuels over that of tires in case 2 is attributed to the high excess air (80-100 percent) employed during the performance tests of the tire-fired boiler. Decrease of this excessive amount can be expected to raise combustion and boiler efficiency.

Nevertheless, in every case shown, the tire-fired boiler shows marked savings over those fueled with oil and gas, even when the higher scrap tire cost is compared with the lowest oil and coal requirements. The advantage of the tire-fired unit is even more striking for the case of the completely depreciated units, where its steam costs range from slightly less than 30 to 66 percent of those units fired with oil or coal.

This, however, does not reflect the total advantage of a tire-fired boiler. This equipment, since it is ecologically oriented, may be depreciated over an 8-year period as contrasted with a 25-year depreciation time for the conventionally fueled units. Table 2 compares costs, taking this factor into consideration, for the first 8 years of operation of equipment designed for the three fuels. Within this time, the tire-fired unit has been completely depreciated while roughly half the investment in the other units remain unrecovered. While such differences increase the relative paper costs of the tire-fired boiler during its first years of operation, a distinct cost advantage for it remains. Indeed, a year-by-year cost analysis for the "worst" case--highest tire cost, lowest coal requirement--shows that accumulative operating costs after 4 years are equal, while undepreciated capital is $150,000 greater for the coal-fired unit.

Another method of comparing relative values among the units is to calculate the prices of alternate fuels, which would give total operating costs equal to that of a reference fuel. In figure 1 are shown the acquisition costs of tires, which would give operating costs identical to a coal-fired boiler burning the minimum fuel requirement. This "value" of tires ranges from $14.35 per ton in the first year of operation to $39.40 per ton in the ninth year, while, after full depreciation of both units, this value dips slightly to $34.70 per ton.

Table 2. Eight-year operating costs at maximum depreciation

	Scrap tires		Oil		Coal	
Capital investment - $ M	1,500		320		800	
Depreciation period	8 years		25 years		25 Years	
Unit fuel cost	$10.00/ton	$20.00/ton	$0.33/gal		$45.00/ton	
Daily fuel requirement	48 tons	48 tons	8,900/gal	6,120/gal	52 tons	38.25 tons
Eight-yr costs - $ M:						
Capital related						
Depreciation	1,500	1,500	168	168	421	421
Interest	500	500	193	193	481	481
Taxes, ins.	360	360	77	77	192	192
Total	2,360	2,360	438	438	1,094	1,094
Operating costs						
Fuel	1,344	2,688	8,224	5,656	6,552	4,824
Labor	520	520	400	400	520	520
Maint. & utilities	280	280	104	104	280	280
Total	2,144	3,488	8,728	6,160	7,352	5,624
Total 8-yr cost	4,504	5,848	9,166	6,598	8,446	6,718
Undepreciated capital	None	None	152	152	379	379

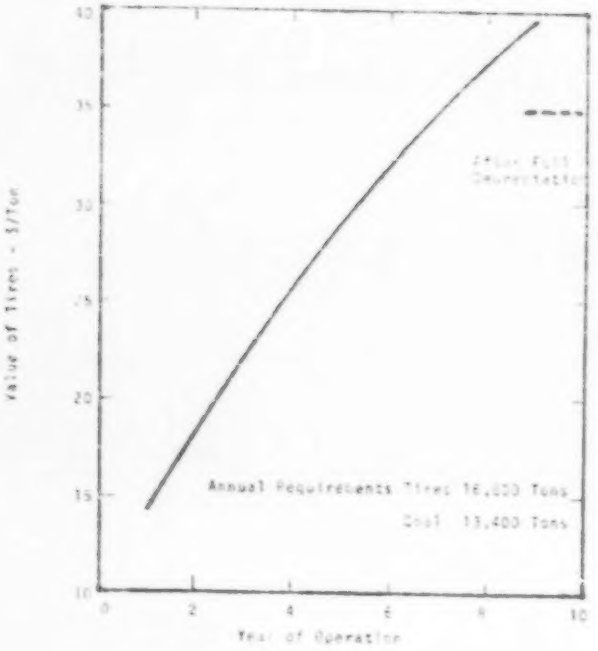

Figure 1. Value of scrap tires vs. coal @ $45.00/ton.

Alternatively, one may set the price for tires under various depreciation conditions, and calculate the prices necessary for oil and coal to equalize the total operating costs. The results of such calculations are shown in table 3. For fully depreciated plants, oil prices of $0.08-$0.19/gallon and coal prices of $10.00-$27.00/ton are required, depending on the comparison made. In all cases these are much lower than the $0.33/gallon for oil or $45.00/ton of low-sulfur coal currently being encountered.

The tire-fired boiler thus meets the needs of the American society today; it generates cheaper steam at no drain on fossil fuel sources while contributing a most viable solution to the disposition of a troublesome solid waste component.

Table 3. "Break-even" fuel costs

Depreciation mode	Fuel costs Tires, $/ton	 Oil, ¢/gal	 Coal, $/ton
I. 25-yr. straight line[a]			
Equal Btu value	10.00	13.0	15.80
	20.00	18.4	25.00
Minimum oil & coal	10.00	18.9	21.40
	20.00	26.7	34.00
II. Maximum depreciation rate[b]			
Equal Btu value	10.00	14.3	17.90
	20.00	19.7	27.10
Minimum oil & coal	10.00	20.8	24.30
	20.00	28.6	36.90
III. Fully depreciated units			
Equal Btu value	10.00	7.7	10.40
	20.00	13.1	19.60
Minimum oil & coal	10.00	11.2	14.10
	20.00	19.0	26.70

[a] First-year operation.

[b] Depreciation period--tires, 8 years: oil and coal, 25 years; average of first 8 years of operation.

Acknowledgment

The assistance of members of the Goodyear Corporate Engineering Department, particularly that of E. R. Moats, was of the highest value in the preparation of this paper.

DISCUSSION

OBSERVER: Mr. Smerglia, did I understand you to say that the desulfurization unit was not used, was not required?

MR. SMERGLIA The desulfurizer is being used, but not being used for the purpose it was intended for. It is not removing much SO_2 because we are not using caustic in the desulfurizer. It is in operation though.

OBSERVER: Do you have any idea at what level the sulfur oxide is coming off the stacks? Do you have any data on it?

MR. SMERGLIA: Yes, we have. They are roughly one-third of the emission standard in Michigan. I haven't been too concerned about that for obvious reasons. It is better than low-sulfur coal, and we are not concerned with that. We have gone just beyond that parameter though. The levels are satisfactory.

MR. MARK L. DANNIS (The B. F. Goodrich Company, Brecksville, Ohio): What happens to the steel?

MR. SMERGLIA: The steel comes out with that ash and gets oxidized. There is quite a bit of iron oxide. The bead actually oxidizes, and it melts and comes off with the ash.

MR. DANNIS: Is it possible to reclaim it? Apparently you haven't done so.

MR. SMERGLIA: I think in the future it might be. With the price of scrap metal, it is highly unlikely that currently it could be employed because the economics just aren't there. Zinc, on the other hand, I am almost sure will be reclaimble, because zinc is becoming very, very short in supply. They were recycling more and more scrap zinc.

MR. JAMES McGARRY (New York State Department of Environmental Conservation, Buffalo, N.Y.): Have you analyzed any particular emissions of this, and if so, how do they compare with a comparable oil- or coal-fired unit?

MR. SMERGLIA: Yes, I made a comparison on that basis, in Dr. Cox's paper here. They are less than 0.65 pounds per thousand pounds of dry gas, which is the standard in Michigan for particulate emissions from a conventional coal-fired boiler with capacities beneath 100,000 pounds per hours. This si the only standard we have to go by in Michigan. There is no applicable standard in Ohio regulations for this type of unit, so we have to go by the conventional regulations.

OBSERVER: Mr. Taggart, I would like to know the size of the boiler you use in the 10 percent mixture of rubber with coal.

MR. TAGGART: There are a total of eight boilers at Fisher Body, and of the two that we did stack tests on, one is 160,000 pounds per hour and the other 80,000 pounds per hour. So one is above 100,000 pounds.

OBSERVER: The cost of rubber is $24.46. Was that the cost of grinding, or was that the delivered cost to you?

MR. TAGGART: That was the delivered cost to us.

OBSERVER: Was that '73 figures?

MR. TAGGART: That was '74 figures.

SCRAP TIRES AND FISHERY RESOURCES

Richard B. Stone*

Abstract

Over 200 million tires are discarded each year. Less than 10 percent of these are reused; the remainder continue to pile up around the countryside creating waste-disposal problems. Research by the National Marine Fisheries Service Artificial Reef Program at Beaufort, North Carolina, has demonstrated that scrap tires are effective, low-cost, artificial reef material. Reefs constructed wholly or partially of scrap tires can provide or improve habitat for fishes and invertebrates in many areas and thereby increase the angler catch per unit of effort. The use of large numbers of scrap tires for artificial reefs could benefit fishery resources and could also offer a partial or temporary solution to the tire disposal problem.

Sport and commercial fishermen reap a large harvest from fishery resources each year. In 1970, commercial fishermen in the United States caught 4 billion pounds (ref. 1), and 9.4 million salt water sport fishermen caught over 1.5 billion pounds (ref. 2). At projected levels of increase in population growth and leisure time, we can expect the number of recreational fishermen to more than double by the year 2000. The future demands on stocks of fishes will necessitate effective management of these resources to maintain or improve angler success.

Scrap tire disposal is a national problem that can only be solved through application of new and more efficient techniques. Scrap tires should be recycled when possible, but that process accounts for less than 10 percent of those that are available. The remainder, more than 200 million per year, continue to pile up around the countryside.

Research by the National Marine Fisheries Service has shown that scrap tires are effective artificial reef material (ref. 3) and that artificial reefs, used properly, are potentially valuable in the management of coastal fishery resources (ref. 4). Therefore, the use of large numbers of scrap tires to develop coastal fishing reefs would benefit fishery resources, and could offer at least a partial or temporary solution to the scrap-tire disposal problem.

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*Atlantic Estuarine Fisheries Center, National Marine Fisheries Service, Beaufort, North Carolina 28516.

Artificial reefs are manmade or natural objects intentionally placed in selected areas of the marine or freshwater environment to provide or improve rough bottom habitat. By increasing the amount of reef habitat, they provide the potential for increasing the number of reef fishes in an area and improving angler catch per unit of effort. Irrespective of the types of materials used to build reefs, the main features that appear to attract marine animals to these habitats are shelter, visual reference points, and food. Artificial reefs also provide some fishes access to new feeding grounds and open additional areas for territorial fishes.

An important feature of reef habitat is the shelter provided by holes, ledges, and dark corners of the irregular substrate. Organisms (e.g., algae, corals, and sponges) that attach to the reef provide additional shelter by increasing the complexity of the habitat. Most fishes become prey animals at one time or another and therefore need places to conceal themselves (ref. 5). By providing shelter and concealment, artificial reefs can increase the survival rate of many fishes and allow more fish to reach a larger size.

The reef profile may be used as a landmark or visual reference point for fishes. These landmarks provide a spatial reference for fishes in an otherwise rather featureless environment (ref. 6). Species that exhibit a strong homing tendency, or those that inhabit a fixed territory, may rely on landmarks to locate or define their territory. Visual reference appears to be important to fishes that make daily movements to feeding grounds; after feeding, many of these fishes return to specific sheltered areas (refs. 7,8).

Some fishes feed primarily on the motile or encrusting organisms associated with reefs, and others forage on the surrounding bottom while depending on the reef for shelter. Their food sources are organisms living in or on the sediment, or in nearby grass beds.

Scrap tires have been used as artificial reef material for many years. In recent years, the single-tire, three-tire, rod-8, and bale-unit (ref. 3) have been the tire unit designs most frequently used in reef construction.

The cost (table 1) of building tire units is extremely variable, but the total cost per tire for two of the more commonly used units (single-tire and bale) is similar to the amount that some tire dealers have to pay to dispose of their tires. The least variable figure for judging tire unit costs is that for materials needed to assemble the units. Groups building artificial reefs may use volunteer labor but normally must pay for most materials, except tires.

If the project is a community effort, much of the material may be donated, and the reef can be built for minimal cost. The cost of transporting materials to the reef may also be minimal, depending on the interest of participants. The prices listed in table 1 reflect 1972 costs for materials and labor and would be reduced by any donations.

The U.S. Army Corps of Engineers has approved over 140 artificial reef sites now located along the East Coast of the United States. More than one million scrap tires have been used on reefs at 80 of these sites. None of the reefs have been constructed as large as originally planned. Actually, only a small portion of the total surface area of the sites contains reef material.

Most of these reefs are not large enough to maintain angler success at a high level as fishing effort increases. To meet immediate demands, many of these existing reef sites are being enlarged. If scrap tires are used to complete the 140 reefs on the East Coast to an average height of 3

Table 1. Approximate costs for four common tire unit designs (1972)

Tire unit	Material & labor/unit	Transportation/ unit	Total cost/ unit	Total cost/ tire
Single	0.26	0.08	0.34	0.34
Three	2.88	1.12	4.00	0.50
Rod-8	0.57-3.00	0.60-1.68	1.17-4.68	0.39-1.49
Bale (9 tires)	0.84	1.26-2.25	2.10-3.09	0.21-0.31

[a] Figures based on no-cost delivery of donated tires to staging area.

feet, a total of about one billion tires would be required. A need for more reefs is anticipated to meet future fishing demands. If tires are only a portion of the material used to build these reefs, several hundred million more tires would be needed. Based on these projections, about one and one-half billion tires could be used on artificial reefs in marine waters off the East Coast of the United States.

Scrap tires are the most popular reef material used because they are readily available at no cost from tire dealers and recappers, are inexpensive to assemble into units, and are relatively easy to transport to reef sites. Tires are durable and, once in place on the reef site, provide an excellent surface for the attachment of encrusting organisms. They do not leach toxic substances into the water (ref. 9) or decompose, as metal, and they are not affected by boring organisms that cause structural breakdown in wood although they are attacked by some bacteria. They have a high ratio of surface area to volume, and the configuration of the tire provides protective niches for motile species.

Like any reef material, tires must be used properly to assure that a reef will not conflict with other uses of the marine environment such as navigation and commercial fishing. If the units are constructed correctly, there should be no movement of materials once they are on the bottom. To construct a reef, a Federal permit is required. In addition, State permits are required in many States (ref. 10). By regulating where and how reefs can be constructed, permits eliminate conflicting uses of the same area of ocean bottom.

The future for habitat improvement with artificial reefs seems bright. These reefs offer a potential for increasing coastal gamefish resources, for improving catches in local commercial and sport fisheries, and for using large numbers of scrap tires until new techniques for recycling become economically feasible.

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DISCUSSION

MR. BILL LANG (The General Tire and Rubber Company, Akron, Ohio): In the papers this morning, there was some concern about the health hazard from tire dust laying along the roadside. In your paper it is quite obvious that the Bureau of Fisheries has not encountered any health hazard in the use of these scrap tires. Should an analogy be made from the marine environment to the dry tire on this health situation?

MR. STONE: I don't think an analogy could be made because the tires in the marine environment virtually do not break down, whereas the tire dust problem is one that is caused by the breakdown from the use of tires on the road.

MR. LANG: But chemically the rubber is not broken down. It has been mechanically grated into small particles of one or two microns, but chemically and physically the rubber has not been decomposed in any manner.

MR. STONE: All right, I understand what you are saying. I am not qualified to tell you whether or not tire dust is chemically inert. Concerning particulate matter in the marine environment, we have conducted controlled studies in the laboratory as well as in the field to determine whether there are possible deleterious effects on marine life from tires. There are none. In our laboratory studies with control and experimental tanks, we found no difference between control fishes and experimental fishes that were subjected to tires in a semiclosed system, where there was water flowing through, but slowly. We conducted this study for more than 3 months to see if there was any possibility that PCB's, pesticides, or heavy metals would be leached from the tires, or if these substances would wash off the immersed tires because they had been picked up during use on the roads. As I said before, we found no difference between the control and experimental animals. A group in Maine chemically broke down tires to see what might be released into the marine environment. The only compound they expressed some concern about--and they really didn't feel that there was a concern, because of the amount that would be released--was zinc, over a long period of time. But the tires virtually don't break down in marine environment, or if this occurs, it occurs so slowly that I don't think that zinc release would be a problem. We took every precaution that we could before we started talking about using scrap tires to make sure that there wouldn't be something released into the environment. Now, as far as the analogy between tire dust and what we found in the marine environment, I'm not sure; I haven't done any work with tires on land. You will have to ask someone else about that.

MR. MARK L. DANNIS (The B. F. Goodrich Company, Brecksville, Ohio): Part of the previous question involves knowing the amount of surface area involved and the temperatures the tires would be exposed to. The marine environment is relatively cool, especially compared to the hot highways, and the surface area of the tire is entirely surrounded by water on the reefs. The oxygen concentration on the bottom of the ocean is considerably less than the oxygen concentration in the open air. All these things tend to make the tire very stable in the ocean. Salt water further decreases the solubility of the organic ingredients over that of pure water extraction.

MR. J. R. LAMAN (The Firestone Tire and Rubber Company, Akron, Ohio): How about taking a little pressure off, and start a question regarding Lake Michigan or Lake Erie.

MR. STONE: I probably should have spoken more on the fresh water environment since this is something that would be of interest to you people. In January I visited the Michigan Department of Natural Resources and attended a meeting of their fisheries division. They are planning to start a reef program for Lake Michigan and some of the other lakes around Michigan. As a matter of fact, they were interested in locating a supply of tires, so I gave them the names of some of the people I know in the tire industry. To give you some examples of what they have done in fresh water, a friend of mine, Eric Prince, at Virginia Polytechnic Institute is studying freshwater reefs, and has been using tires and brush shelters in this work. He has found that catches of fishes over artificial reefs are greatly improved for many species including bass, which is the fish many anglers are most interested in. You would be surprised how many freshwater reefs now exist. Many of the States have done work on freshwater reefs, not necessarily because of tire disposal, but because the catch over these reefs is greater than it is over other areas in the lake. So to answer your question, yes, there is a good chance that within the next few years you will find a number of reefs and probably tire reefs in Lake Michigan and you would be surprised how many freshwater reefs already exist.

RATIONALE, SCOPE, AND SPONSORSHIP OF ACADEMIC PROGRAMS

Louis S. Beliczky M.S., M.P.H.*

A 2-day conference on enviromental health factors related to chemicals used in producing polymers, and the use of the polymers and other chemicals in the manufacture of rubber and plastic products, has preceded this session.

This morning's proceedings will relate to the United Rubber Workers' (URW) negotiated joint occupational health program, which was negotiated about 5 years ago. It is considered to be a historic first in organized labor involving a union, a company, and a university--a historic first in the labor-management contractual commitments in the area of workers' environmental health.

The joint occupational health program was negotiated about 130 years after Charles Goodyear's discovery of the vulcanization process in 1839. The first company in the United States to manufacture rubber articles was the Roxbury India Rubber Company, established in Roxbury, Massachusetts, in the year of 1832. By the year of 1849, New England was the site of 36 companies that employed some 3,000 workers involved in the manufacture of waterproof cloth, rubber soles, and boots.

Eight years after Dr. Benjamin Franklin Goodrich opened the first rubber factory in Akron, Ohio, in 1871, there were about 140 companies providing employment for about 12,000 workers. At the end of World War I, about 160,000 workers were employed in about 500 work places. World War II war effort production peak was at a level of 180,000 workers. Curtailment of crude rubber availability during the early years of World War II spearheaded the development of synthetics: butadiene, neoprene, Thiokol, and others. U. S. Government synthetics programs at that time established the so-called GR rubbers, which are still used at the present time: GRS, which is a butadiene styrene copolymer; GRI is a isobutylene and butyl polymer rubber; GRM, the Du Pont neoprene made from chlorobutadiene; and GRP is Thiokol.

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*Director of Industrial Hygiene, United Rubber Workers International Union, Akron, Ohio.

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Monomers are initiators of polymerization reactions. We must all be aware of the current health hazards related to vinyl chloride--the monomer used to make the polymer PVC Resin. If we look at the chemical configuration of vinyl chloride and relate it to the chlorobutadiene structure, we understand the significance of recent data informing us that four Russian papers published during 1968 to 1972 have implicated chlorobutadiene as the causative factor in production of lung and skin cancer among workers in parts of Russia, including Armenia. Du Pont made these reports available to the Assistant Secretary of Labor and the Director of the National Institute for Occupational Safety and Health in December 1974. The monomer chlorobutadiene is used in the polymerization of neoprene, which is used extensively in footwear and industrial products facilities organized by the URW. As with PVC Resin, the residual monomer in the polymer must be considered to be a potenially hazardous carcinogen.

In the past, as with vinyl chloride, chlorobutadiene was considered to be toxic, and was assigned a TLV of 25ppm based on its effect on the liver.

Our concern with monomers similar to vinyl chloride therefore becomes apparent. Carbon chain molecules which could be split to vinyl chloride from either vinylidene chloride or chlorobutadiene and their potential as human carcinogens must not be neglected.

Our concern, therefore, is a real one. The University Programs that will be discussed later have applied their epidemiological, mortality, and morbility data to assess the worker hazards involved in the production and use of the polymers and copolymers currently used by industries involved in the research-oriented negotiated Joint Occupational Health Programs.

For about 135 years, workers have been exposed environmentally to many chemicals that are used in the rubber industry. Rubber recipes became more complex than just that for crude rubber and its relatively simple blends made many years ago. Complex chemicals and molecules became accelerators, antioxidants, antiozonants, retardants, modifiers, and extenders. Inorganic fillers and rubber lubricants, such as asbestos, free silica, clay soapstone, mica, talc, and lead found their way into the industry. Complex tackifiers, cements, solvents--especially benzene--became routine in production operations.

The use of many rubber and plastic compounding chemicals has increased during the years. Their formulations have become complex and will become even more complex as time goes on. The simple formulations used to produce buggy tires about 85 years ago have become chemical complexities with the advent of pneumatic tires in the early 1900's. As our technology improves the rubber and plastic products, the number of chemicals used in the manufacturing processes increases.

Worker health issues and the exposure of workers to certain chemicals did not become matters of great concern until recent years. Periodically a catastrophe would highlight the environmental danger of workers' exposure to materials used in this industry: the napthylamines and the production of cancer of the bladder, benzene and the leukemias and lymphosarcomas, and nitrile's effect on the central nervous system.

Large corporations, the Rubber Manufacturers Association, and the unions were not fully cognizant of the complex variables overshadowing the health of the worker. The worker and his work environment in the plant were, and sometimes still are, generally ignored. Why, for 85 years, are we still unaware of the composition of curing room fumes? Why is good toxicological information regarding the many chemicals used in the industry still lacking? Why do we have complex and serious environmental health problems and the deaths which speakers from Harvard and the University of North Carolina will discuss?

Why was it necessary for a union to negotiate university research programs? Why should it have taken 85 years for such studies to be undertaken?

URW International President Peter Bommarito negotiated the current joint occupational health program, which you will hear about soon. He did not know why rubber workers appeared to have more health problems than other people in the manufacturing industry.

He felt that more had to be done to preserve the health of the workers he represented. He felt that schools of public health, specializing in occupational health programs, could provide answers and hopefully solutions to the problems he sensed were eroding the health of the workers.

Why so little was done in these areas is not really related to economic issues. The answer to why is probably related to irresponsible action of employers who were reluctant to assume their responsibility. The responsibility belongs to three sectors: the union, the employer, and the scientific communities. Only by such tripartite involvement can we realistically provide the workers with that safe and healthful work environment to which they are entitled.

In 1970, beginning in June and ending in September. Mr. Bommarito led a militant crusade to negotiate what we call a long-range program for the comprehensive study of the workers' health in our plants. The first contract was consummated in July of 1971 by the signing of a contract with the B.F. Goodrich Company, United Rubber Workers Union, and the Harvard School of Public Health. The program in essence relates to retrospective and prospective epidemiological studies, some involvement in toxicological evaluations, industrial medical evaluations, and industrial hygiene studies related to the workers' exposure to chemicals that are used at the worksite.

The initial thrust of the studies were epidemiological, relating directly to the use of death certificate data, insurance company records, social security records, and union records that relate to the cause of death.

The death certificate data produces mortality rates which are investigated so that causes of death may be established. This information becomes necessary to establish surveillance and control programs through environmental engineering and medical studies.

After the signing of the first tripartite agreement in July of 1971 with Harvard's School of Public Health, contracts were signed with the other large rubber companies with both the University of North Carolina's and Harvard's Schools of Public Health.

Harvard is now actively involved with The Armstrong Rubber Company, The Mansfield Tire Company, as well as B.F. Goodrich. Goodyear, Firestone, Uniroyal and General Tire are all under contract with the University of North Carolina.

Both Universities have produced information which is being currently applied to improve the health of workers not only in the URW, but other workers similarily employed not only in the United States and Canada, but also around the world. Publications in scientific journals in this country and Europe attest to the historic scientific and practical significance of the URW-negotiated Joint Occupational Health Program for workers everywhere.

The negotiated program involving primarily those companies with whom we have Master Contracts directly covers about 90 of our local unions and approximately 90,000 members.

With the companies setting aside 1/2 cent per hour per worker employed, about $900,000 is expended annually through contractual commitment. The commitments by all three parties involved are unique as well as historic--and the commitment on the part of the university is motivated beyond just research and has become one of dedication and academic fulfillment, with resultant benefit to all parties involved, especially the worker.

The negotiated programs not only have provided financial support to the universities and sustained the teaching capabilities of the schools, but have also produced a substantive faculty commitment through interdisciplinary involvement of various departments of the school.

Although this country has been involved in the manufacture of rubber products since 1839, the real breakthrough involving worker health problems has been within the last few years and will be discussed by Dr. R. Harris of UNC and Prof. William Burgess of Harvard.

UNIVERSITY OF NORTH CAROLINA OCCUPATIONAL HEALTH STUDIES PROGRAM*

Robert L. Harris, Jr., Ph.D.†

Abstract

Occupational health studies, which were begun in the rubber products manufacturing industry about 2-1/2 years ago by the Occupational Health Studies Group in the School of Public Health, University of North Carolina, are now beginning to yield results. Findings on mortality experience and some characteristics of environmental exposures in the rubber industry are now being reported. Most noteworthy findings to date relate to malignant neoplasms, particularly to cancers of the lymphatic and homatopoietic systems, stomach, bladder, prostate, and respiratory system. Particular attention will now be given to identifying environmental agents or exposure conditions that may be related to findings of adverse health effects.

Introduction

In its master contract negotiations of 1970, the United Rubber Workers Union (URW) and six major rubber-products-manufacturing companies in the United States agreed to undertake joint occupational health programs. Each URW-company agreement provides for establishment, at a school of public health, of an occupational health research group to implement the occupational health research program. Each agreement also provides that the company shall make available to the occupational health research group data and information necessary for its studies and, when existing data are inadequate, that the research group may conduct studies at company locations covered by the agreement.

Between October 1971 and July 1972, agreements were reached between the URW, the Goodyear, Uniroyal, Firestone, and General companies, and the School of Public Health, University of North Carolina, for occupational health studies to be undertaken among the four companies by the school's Occupational Health Studies Group. Some 60 manufacturing plants with a total work force of about 65,000 persons are covered by the agreements between URW and these four companies. Our research group, under each agreement, reports its findings to an Occupational Health Committee comprised of officials of the URW and the companies.

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*Adapted from a presentation at ICF Health and Safety Conference, Geneva, Switzerland, October 29, 1974.

†Director, Occupational Health Studies Group, School of Public Health, University of North Carolina, Chapel Hill, North Carolina 27514.

The long range objectives of our Occupational Health Studies Group in the research under these agreements are:

1. The identification of work-related illness and their precursor health conditions;
2. The identification of environmental hazards related to these adverse health conditions and development of means for their elimination or control;
3. The development of recommendations for surveillance of health status and environmental conditions to permit early detection of health problems or hazards so corrective or preventive actions may be taken.

Organization and Facilities

For projects within each company there is a research team comprised of an epidemiologist, an industrial hygienist, a biostatistician, and research assistants. Most of these scientists hold appointments in either the Department of Epidemiology, Environmental Sciences and Engineering, or Biostatistics in the School of Public Health.

A Policy Board, appointed by the Dean of the School, meets at regular intervals to consider problems and prospects of the Study Group and advises the director and the dean on matters it considers pertinent to the success of the research effort.

The Study Group has access to laboratory facilities equipped with a variety of analytic instruments and a complement of industrial hygiene field equipment. These are ordinary industrial hygiene laboratory instruments used to measure concentrations and assess composition of gasses, vapors, and fine particles. The group also has within its offices a computer terminal which has access to two large high-speed digital computers (IBM 370/165; IBM 360/75).

Projects Underway

The emphasis in the initial epidemiologic research has been in mortality studies among populations of workers drawn from the agreement plants. By using a variety of sources of information such as the records of unions, companies, insurance carriers, and the Social Security system, the fact of death of persons in selected cohorts of workers can be learned. Death certificates can then be obtained in almost all cases, and the underlying causes of death can be determined. The listed causes are nosologised to the International Classifications of Diseases codes to permit comparision with National and other cause-of-death statistics that use this code system. In those cases wherein a population at risk can be sufficiently well defined, cause-specific death rates can be determined; several projects of this type have been completed, and others are underway. Proportional mortality analyses, however, can be done with data on deaths only. In such studies the ratios of specific causes of death to total deaths in a worker group can be compared with ratios for the same causes to total deaths in the general population or other comparison groups. Several such analyses are underway, and on some of these results are available.

Records covering the 9-year period 1964-1972 for one group of approximately 7,000 male rubber workers have been examined for cause-specific death rates, and the results have been reported (ref. 1). As shown in table 1, the overall death rates were very near the expected values when compared with United States equivalent population experience for both age ranges examined (40 to 64 years and 40 to 84 years). Some causes, however, appeared in greater than expected rates. In this, and in subsequent tables of the same type, the "expected ratio" has the value "one.

Even using the conservative approach of comparison with overall U.S. death rate statistics, which ignores the fact that worker groups are selected groups and in the absence of work-related health hazards are healthier than the general population, some causes of death appeared in noteworthy excess. For the causes shown here, excesses were generally greater among the younger, working-range, age group than for the total age range considered, which includes retirees. Especially noteworty are

Table 1. Standardized mortality ratios, selected causes of death
(One tire-manufacturing plant, 1967-1972)

Cause (I.C.D. Code)	40-84	(Deaths)	40-64	(Deaths)
All causes	0.99	(1783)	0.93	(489)
Stomach cancer (151)	1.87	(39)	2.19	(12)
Large intestine cancer (153)	1.23	(39)	1.21	(10)
Prostate cancer (185)	1.42	(49)	1.47	(6)
Lymphosarcoma (200)	2.26	(14)	2.51	(6)
Leukemia (204-207)	1.28	(16)	3.15	(11)
Diabetes mellitus (250)	1.43	(43)	1.57	(13)
Arteriosclerosis (440)	1.54	(34)	2.23	(4)
Liver cirrhosis (571)	1.22	(35)	0.78	(14)

leukemia and stomach cancer. This is an initial analysis of the data; we recognize that examining data for a total worker population may obscure noteworthy experience for groups within the population. Analysis of the data for this population by occupational class is underway. We are able also to examine the data by dates and duration of each job held.

Age-standardized, proportional mortality ratios were determined for each of six plant populations, which includes the plant for which the foregoing death rate determinations were made (table 2). Even in the summary data for the six plants, higher than expected ratios were revealed for various cancers among the listing of deaths of workers from these plants.

Again, the ratios for cancers of the stomach, prostate, and lymphatic and hematopoietic systems (the group which includes lymphosarcoma and the leukemias) appear in greater than expected ratios, and again the ratio for cancers of the respiratory system and the bladder are higher than expected among the working age range. In three of the smaller plants, an excess of cancers of the central nervous system is suggested.

This pattern is generally repeated in other proportional mortality analyses done to date. Results of these studies have not yet been published. In a group of four tire-manufacturing plants, higher than expected ratios of cancers of the stomach, the bladder, and the lymphatic and hematopoietic tissues are noteworthy (table 3).

Table 2. Age-standardized proportional mortality ratios for selected cancers

(Six tire-manufacturing plants, 1964-1972; total deaths = 2469)

	Age range	
Cause (I.C.D. code)	40-84	40-64
Stomach cancer (151)	1.58	2.06
Respiratory system cancer (160-163)	1.10	1.18
Prostate cancer (185)	1.09	1.88
Bladder cancer (188)	0.98	1.28
Lymphatic and hematopoietic cancer (200-209)	1.26	1.67

Table 3. Age-standardized proportional mortality ratios selected cancers

(Four tire-manufacturing plants, 1963-72; total deaths = 2289)

	Age range	
Cause	40-84	40-64
Stomach	1.60	2.08
Respiratory system	1.10	1.11
Prostate	0.92	1.15
Bladder	1.54	1.48
Lymphatic and hematopoietic systems	1.24	1.18

In addition to the cancers listed here, the ratios for deaths from emphysema and cirrhosis of the liver are high for some plants. In preliminary and yet incomplete data for two additional plants, these causes again appear in ratios higher than expected, along with an indicated excess for prostate cancer as was found in other larger studies (table 4).

Analysis for cause-specific death rates and proportional mortality ratios are continuing. Specific effort is being devoted to relating types of work experience to specific causes of death which appear in higher than expected numbers. Several study populations are being examined for cause-specific death rates by occupational category and by date and duration of jobs held. Findings of such analyses may identify high-risk job categories for any disease category.

Case control studies to identify high-risk occupations have been initiated or are being developed for diseases such as leukemia, bladder cancer, and stomach cancer, which have appeared in greater than expected ratios among all or most of the study populations. The first of these from which results are available is a study of leukemias and similar

Table 4. Age-standardized proportional mortality ratios selected cancers

(Two tire-manufacturing plants, 1964-72; total deaths = 217)

	Age range	
Cause	40-84	40-64
Stomach	1.89	3.70
Respiratory system	1.02	0.95
Prostate	1.59	1.56
Bladder	1.33	(no deaths)
Lymphatic and hematopoietic systems	1.83	1.76

cancers (ref. 2) (table 5). Deaths resulting from diseases within this group among males from one plant were examined. Most noteworth, lymphatic leukemia in the 40-64 year age range yielded a seven-fold excess. Smaller excesses were noted in other categories. Data for these deaths were combined with those for several smaller plants and examined for any relationship between deaths from these types of cancers and work history. Work experience for 88 cases of death from leukemia and similar cancers are compared with histories for 264 matched controls from these plants to determine if differences in occupation could be detected. In six occupational categories, the proportion of man-jobs among cases exceeded the proportion for controls by one-half or more (table 6). The greatest difference was in Repairing Tires.

The various occupational categories were combined into groups judged to have exposures to solvents and those judged not to have such exposures.

Table 5. Age-standardized mortality ratios cancers of the lymphatic and hematopoietic systems

(One plant, males, 1964-72, 36 deaths)

	Age range	
Cause	40-84	40-64
Lymphosarcoma and reticulum cell sarcoma	1.42	1.74
Hodgkins disease	2.21	0.92
Other lymphoid tissue neoplasms	*----	----
Multiple myeloma	0.64	----
Lymphatic leukemia	2.11	7.64
Myeloid leukemia	1.02	2.04
Monocytic leukemia	----	----
Other and unspecified leukemia	0.38	----
Polycythemia vera	----	----
Myelofibrosis	----	----

*No deaths.

Table 6. Proportion of jobs held, lymphopoietic cancer cases and controls, for selected occupational titles

(Seven plants, deaths 1964-72, total man-jobs = 5800)

Occupational title	Case percent	Control percent	Ratio
Synthetic plant	2.1	1.1	1.9
Tuber service-tread	2.3	1.4	1.6
Roll changing	2.5	1.1	2.3
Maintenance-electrical	1.0	0.5	2.0
Industrial products	1.5	0.6	2.5
Repairing tires	1.5	0.2	7.5

Analysis for all cases (88 cases) and controls revealed no statistically significant differences. Analysis of 17 cases of lymphatic leukemia and their matched controls, however, showed a significant difference between cases and controls in the amount of time spent in solvent exposure jobs. On the average, a lymphatic leukemia case spent 11 years in jobs involving solvents while the matched controls spent 4 years in such jobs. The cases spent less time than did the controls in jobs not involving solvent exposures. The greatest difference in solvent-exposure job patterns of the lymphatic leukemia cases and their controls was the Tire Repair category, and work experience in jobs listed as involving solvent exposures in this case group has all been since 1945.

A case control analysis of data on colorectal cancer among the same population failed to reveal a statistically significant association of any occupational group with the disease. Although statistical significance was not achieved, the results suggest the possibility of associations of colorectal cancer with mixing, milling, plant maintenance, and machinists. Such associations merit scrutiny in other studies underway.

Compared with mortality sutdies, morbidity studies often must be done with less adequate records, with sparse information on experience for a normal comparative population, and are generally higher in cost to perform. The matter of occupationally related morbidity has been addressed in our study group through two types of studies, records analysis and current health status investigations. In the first category is an analysis of cause specific disability retirements from large tire-manufacturing plants (table 7). Examination of 271 disability retirements over the interval 1963-1972 revealed higher than expected levels for retirements for skin and musculo-skeletal diseases, and to a lesser extent for respiratory and endocrine system problems, when compared with Social Security Administration data for disability retirements from all occupations in the United States. The higher than expected number of retirements for respiratory disease appears to be related to a specific episode at the plant in the early 1960's.

Table 7. Age-standardized proportional disability ratios (One plant, 271 retirements, 1963-72)

Datum: Social Security Administration disability awards, all occupations

Cause or disorder	SPDR
Infections	0.13
Neoplasms	0.75
Endocrine	1.33
Blood	*----
Mental	1.17
Nervous	0.50
Circulatory	0.76
Respiratory	1.43
Digestive	0.94
Genito-urinary	----
Skin	11.78
Musculoskeletal	2.37
Congenital malformation	----
Ill defined and accidents	0.76

*No retirements.

A study of sickness absence in the same plant for the period 1944 to 1972 failed to reveal any remarkable association of such absence with work experience except for the respiratory illness episode of the early 1960's, which was mentioned earlier.

Health status studies involve both the administration of questionnaires to workers to learn from them of their health experience, and the conduct of selected health status examinations. Questionnaire surveys have been made among workers in two large plants, and among selected groups in a third plant. Work is still underway to assess the questionnaire responses relative to other available health status data. The questionnaire surveys have been coupled with health examinations which may include pulmonary function tests, chest X-rays, blood and urine analyses, and medical occupational histories. One such study has been done in a large tire-manufacturing plant, but analysis and reporting of results are not yet finished. A second comprehensive study of this type was done last fall as a joint effort with the National Institute for Occupational Safety and Health in a large plant which involves polyvinyl chloride operations and tire manufacturing.

Several years ago Dr. Mastromatteo reported on pulmonary disease among workers using a resorcinol-methylene donor bonding agent in tire manufacturing. The methylene donor was believed to be the culprit, and use of the system was discontinued. Such systems are again in use with a different methylene donor. A special investigation to determine whether use of resorcinol-methylene donor adhesive systems, currently used in tire manufacturing, may cause respiratory disease was begun last August. Occupational and medical histories were obtained, and pulmonary function tests were performed on persons exposed and matched controls totaling about 250 persons. Environmental sampling for resorcinol, formaldehyde, ammonia, cyanide, and respirable particulates was done at workplaces during the time of the pulmonary function survey. Statistical analysis of the data has just been completed; results will be reported to our committees next week. Although there are some positive findings, I can report that the pulmonary function investigation to date has not demonstrated the serious respiratory effects with presently used materials, which were reported to be associated with the chemical systems used earlier. On the environmental side, measured exposure for none of the contaminants sampled were near threshold limit values.

Initial environmental activities in the program have involved orientation and familiarization with the industry through site visits at a number of plants and fairly intensive investigations at a few selected plants. Job terminology varies from company to company, and from plant to plant within companies. From the environmental work has come a systems of job classification that is used in the epidemiologic work, the health status studies, and in the environmental programs. Through uniform use of such a classification system, results between projects can be compared and medical and environmental findings can be related.

Environmental sampling to date has revealed the expected large variety of exposures to chemical and physical agents, but thus far has not revealed remarkable, consistent excesses over threshold limit values for individual agents. Our primary interest in the environmental work, however, is not in generation of data for comparison with threshold limit values, but in developing information which may help reveal agents responsible for adverse health effects. At the present time we are trying to identify jobs involving exposures to volatile materials, principally solvents, using a variety of means including charcoal tube personal samplers, and to respirable particulates such as carbon black aerosol, dusts in compounding areas, and curing fume, using personal samplers with cyclone presamplers. These results can be coupled with the characteristics and effectiveness of controls in use at the time of sampling.

Samping can represent only current conditions while medical studies represent the results of accumulated experience, perhaps over many years. There is a dearth of quantitative information on past environmental conditions in the rubber industry, but in our environmental work we continue to seek qualitative historical information. Such information will be of value in interpreting epidemiologic findings. Results of current sampling, however, will be of value in future epidemiologic investigations.

The composition of effluents from the curing process has been of particular interest. Initial examinations have shown that the benezene soluble portion, generally representing the organic fraction of particulate material, comprises from about 20 percent to 80 percent of the total particulate, with a median value of about 50 percent. Most of the organic material is near neutral in pH, though some 2 to 5 percent is basic and about 1 percent is acidic. Earlier in this conference, Dr. Stephen Rappaport reported to you on his investigations of emissions of volatile materials from curing of a tread stock. In his work, the C_6 to C_{25} vapors emitted from the curing of a typical tread stock in laboratory apparatus were analyzed qualitatively and quantitatively by gas chromotography and mass spectrometry. Compounds identified included styrene, butadiene oligomers, alkyl benzenes and naphthalenes, and several specific nitrogen- and sulfur-containing substances. Most of these were traced to individual formulation ingredients, i.e., the polymers, an aromatic oil, an antiozonant, and an accelerator. Air concentrations for compounds later confirmed in a curing area (a passenger-tire press room) ranged from a high 1.5 ppm to 5 ppb and varied inversely with boiling point; thus the more abundant substances appear to be in the C_5 to C_8 boiling range. A dimer of butadiene, 4-vinyl-1-cyclohexene, was found to be quite abundant in the curing emissions and appears to be responsible for the characteristic odor of the tread stock.

Plans and Prospects

A number of retrospective mortality projects are underway and will continue with particular emphasis on mortality experience by specific disease and occupational categories. Results of such projects will be used in the search for environmental agents of exposures which may be associated with the diseases found to be in excess. Disease-specific, case-control studies will be initiated as well to identify occupational categories or exposure conditions which may be related to excess disease. In like manner, health experience-work experience relationships will be examined in morbidity and health status studies in efforts to identify occupational or exposure groups which appear to be at high risk.

Environmental surveys to establish a baseline for current environmental conditions will continue, and, as medical studies reveal occupational or exposure groups with adverse health experience, special effort will be made to identify agents or exposures that may be related. This will involve consideration of past exposures as well as current conditions.

As agents or exposures are identified with health problems, the matter of control techniques to eliminate the hazard will be addressed.

Summary

Occupational health studies which were begun in the rubber-products-manufacturing industry about 2-1/2 years ago by the Study Group in the School of Public Health, University of North Carolina, are now beginning to yield results. Findings on mortality experience and some characteristics of environmental exposures in the rubber industry are now being reported. Most noteworthy findings to date relate to malignant neoplasms, particularly to cancers of the lymphatic and hematopoietic systems, stomach, bladder, prostate, and respiratory system. Particular attention will now be given to identifying environmental agents or exposure conditions which may be related to findings of adverse health effects.

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DISCUSSION

DR. CARL A. NAU (Texas Tech University, Lubbock Texas): Would you define, for the benefit of the group, what you mean by control group? Would you mind explaining just how you get your control group?

DR. ROBERT L. HARRIS, JR. (University of North Carolina, Chapel Hill, N.C.): In the case-control studies, where control groups are used, the cases and controls are matched by age, sex, type of work, etc., with controls having died from causes other than causes being examined among the cases. They are drawn from the same population at risk as are persons having the specific diseases being examined.

MR. MARK L. DANNIS (B.F. Goodrich, Akron, Ohio): You stated there were some cases or good examples where enterprise benefits or longevity--that is mortality rate-are much lower than the population as a whole encountered. What might those be, and do you have any idea of the cause?

DR. HARRIS: I am sure there are causes that can be known. I can look at some of these here.* Cancer of the rectum, for example, has an SMR of 60 compared with 100, and cancer of the pancreas has an SMR of 62 in the working age-that is, in the under-64 age group--while in the total age range the SMR is 86. I mentioned cancer of the bladder in some populations. This does not appear in all the populations, but in this particular group, cancer of the bladder had an SMR of 80 rather than 100. Here is an SMR of 78 for liver cirrhosis in the under-64 range, which goes to 122 in the total age range, up to 4 years. It appears that the older people have the excess. Accidents, poision, and violence in this particular group is a 59 rather than the 100. Perhaps a reason, which I suspect may have been discussed here, is the healthy-worker phenomenon. With a healthy-worker group--those who might be considered to be in a relatively nonhazardous type of occupation--one can find the SMR, age--adjusted, in the order of 60. We have done this in looking at one very large group of people who do not have overt identifiable major occupational health insults. If, in these studies, one corrects for active workers not involved for example, you find SMR like that. It may be, in the absence of certain types of insults, that one expects a lower value than one gets in the total population, which includes all occupations and the ages, the well, the infirm, and the institutionalized, etc.

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*Reference to McMichael et al., JOM, 1974 (ref. 1 of paper by Robert L. Harris, Jr.)

MR. LOUIS S. BELICZKY (United Rubber Workers International Union, Akron, Ohio): I think this has been apparently observed in industrial populations and represents a selection constant of "the healthy worker" by the University of North Carolina. I think sometimes we get the feeling, because of that statistical statement and because the SMR may be a bit lower, that it really is healthier to work in one of the plants than not to work in one of the plants, that this is something found as a matter of fact. The workers are selected and given a medical examination.

MR. DAVID CASINE (The Firestone Tire and Rubber Company, Akron, Ohio): I am not knowledgeable, so I would like a layman's comment. Would you say that the rubber industry is a hazardous occupation?

MR. BELICZKY: Based on the information that I have, from my experience related to the mortality studies, not necessarily to morbidity studies, I think that this particular industry has problems of great concern. I have spent much of my time in plants in the United States and Canada, and I am aware of some of the problems. These are my personal feelings; perhaps Dr. Harris would like to express his.

DR. HARRIS: I think that it is really what we are trying to examine here. You ask if it is a hazardous industry; I suppose one could address that question to almost any industry. There may be processes and operations that merit corrections to make it a healthier industry, which the company, the unions, and we are all striving to identify. One purpose of our effort is to get an answer to the question you just asked.

MR. DANNIS: I understand that you have been working on this for 4 years now, going on 5. What kind of timetable do you anticipate that you will come up with factual, meaningful information that could be used by EPA people for rules and regulations?

DR. HARRIS: We have not really addressed the studies to use by EPA people for rules and regulations. We have to address them to the charges that were given by the union-company committee to us, which are to conduct epidemiological environmental studies within this industry to report the findings to them, and we are engaged in that. We have reported some, and we will continue in the research design. We have a responsibility to report to the committees and to the scientific community through publications. If, in turn, these publications become of use to people of EPA and others, it will be their drawing from the studies, rather than our directing studies specifically to their needs. I don't know what their time schedule would be or whether they will gain from our work things that they would use in this area. I just don't know.

MR. BELICZKY: I would like to pick up where Dr. Harris left off. It was never intended that the information gathered here would be directly applied to any regulatory agency, especially EPA. If it has any application in areas of health standards, it may currently be involved with NIOSH--National Institute for Occupational Safety and Health. I think it could have bearing if at any time EPA does become involved with the Toxic Substances Act. To date the data and information that have been gleaned from the university programs had a direct bearing on the establishment of the OSHA current standard on vinyl chloride. The epidemiological studies at the Firestone plant and some of the epidemiological evaluations and publications that were generated by looking at death certificate data at the B.F. Goodrich plant at Louisville certainly have been valuable. The high incidence of cancer of the brain related to vinyl chloride exposure is an example. Currently, the University of North Carolina has been directly involved in the first quadripartite study involving the University, the union, the company, and NIOSH. Comprehensive studies were conducted of workers exposed to vinyl chloride at a facility that both manufactures the polymer and uses the polymer to make film sheeting. In this regard I think there will be some direct input in relating to the standards on vinyl chloride. However, the regulation on vinyl chloride becomes effective on April 1. I think the prime function of the university study is to gain information that would control work exposure to various chemicals, and which would lead us to initiate action to control workers' exposure both environmentally and through medical-surveillance programs. Actions are intended to increase the life span of workers involved in the manufacture of rubber and plastics products.

Harvard's work with talc exposures will lead to a change in the current A.C.G.I.H. TLV for that material.

DR. HARRIS: I have one brief comment here. There is work, as most of you are aware, elsewhere than in the university programs. Work has been underway in Great Britain for some time, and there is a fairly recent publication in the British Journal Industrial Medicine, reporting some standardized mortality ratios in their studies; these ratios have some parallels to what seems to be developing in the studies in this country. Most remarkable are the apparent excesses in neoplasms among the populations studied. So this type of work is underway in other programs as well.

THE RUBBER WORKERS STUDY AT THE HARVARD SCHOOL OF PUBLIC HEALTH

William A. Burgess, John M. Peters,
and Richard R. Monson*

Abstract

The interest by workers on the effect of chemicals and working conditions on health has resulted in three-way agreements between the major rubber companies, the United Rubber Workers, and schools of public health. The Harvard School of Public Health signed agreements with the B. F. Goodrich Company and the Armstrong Rubber Company, with the International Union of Rubber Workers as the third party.

Under these agreements the Occupational Research Study Group at Harvard conducts epidemiological studies of potential health hazards and in-plant investigations of exposure to air contaminants. The Study Group also assists in the development of safe standards for occupational environments and environmental controls. The Harvard Study Group is represented by faculty members of the Departments of Environmental Health Sciences, Epidemiology, and Physiology.

To uncover possible unknown occupational health problems, a major mortality study has been conducted. This study has demonstrated excess stomach cancer in processing workers, excess lung cancer in tire-curing workers, and excess bladder cancer and leukemia in the general plant population.

In a parallel effort, detailed occupational health surveys of each plant by a Harvard physician-engineer team revealed specific company-wide problems, which deserve further research. These studies, which are complemented by laboratory investigations, include the exposure of curing press operators to various off-gases and fumes from the process, the hazard from processing dust, and the exposure to industrial talc.

William A. Burgess, Associate Professor of Occupational Health Engineering; John M. Peters, M.D., Sc.D. (Hyg.), Associate Professor of Occupational Medicine; and Richard R. Monson, M.D., Sc.D. (Hyg.), Associate Professor of Epidemiology, Harvard School of Public Health, Boston, Massachusetts 02115.

INTRODUCTION

Mr. Beliczky traced the history and background of the three-way occupational health agreements in the rubber industry, which have been recognized as hallmark collaborative programs. Under this program the Harvard School of Public Health signed agreements with the B. F. Goodrich Company and Armstrong Rubber Company, with the United Rubber, Cork, Linoleum and Plastic Workers of America in each case being the third party.

The program, which is financed by special contributions by industry, is administered by an Occupational Health Committee (OHC) composed of three management and three union representatives. The Occupational Health Committee reviews and approves the research plans proposed by the university research team, makes recommendations for the implementation of the findings of the research, and reviews occupational health problems referred to it by local plant Health and Safety Committees for possible referral to the university.

Under the agreement, an Occupational Research Study Group (ORSG) was established at the university. This research team conducts epidemiologic studies and in-plant investigations to define potentially hazardous conditions. The Occupational Research Study Group also assists in the development of safe standards for occupational environments.

At Harvard the ORSG includes members from the Departments of Environmental Health Sciences, Epidemiology, and Physiology.

The Harvard program includes mortality studies to define possible unknown health hazards. Joint medical-industrial hygiene studies of plant populations are also conducted to elucidate the effects of known potentially hazardous materials or conditions. The latter studies are supported by extensive laboratory research programs. Selected studies in each of the above program areas will be described in this paper.

EPIDEMIOLOGY

In one study the mortality experience of approximately 24,000 past and current employees from one plant in Ohio going back to 1935 has been reviewed by Monson and Nakano of the Department of Epidemiology. Starting in October 1971, mortality data were collected from three primary sources--the dues files of the union, the employee file maintained by the company, and the death file maintained by the company. The data were supplemented by death certificates obtained from the company insurance carrier and from the Ohio and other State health departments. Information on the vital status of terminated employees was obtained with the assistance of the Internal Revenue Service and the Social Security Administration.

A comparison was made between numbers of deaths observed among rubber workers as compared to numbers of deaths expected on the basis of United States death rates. In this comparison, race, sex, age, and time were taken into account. Comparisons were made for all rubber workers, as well as for groups of rubber workers who had worked together in specific areas of the plant.

The mortality experience between January 1, 1940, and June 30, 1974, of 13,571 white male employees at this single plant revealed that mortality was between 62 percent and 82 percent of that expected based on United States death rates. With the exception of cancer, there was no strong indication that there were excess deaths from any specific cause of death. There was an indication of excess deaths from specific cancers among workers of a number of different departments, as shown in tables 1 and 2.

1. Excess gastrointestinal cancer was seen in all age categories and was greatest in processing workers who died at age 75 and above.

2. Excess lung cancer was limited to tire-curing workers who started work between age 25 and 34 and who died in 1955 or later.

3. Excess bladder cancer was greatest in men who worked at least 35 years and who died at age 75 or above. No excess risk was present in men who started working after 1934. (In men who started working between 1930 and 1934, there were 7 deaths due to bladder cancer and 5.1 expected.)

4. Except for age started working, the patterns for lymphatic cancer and myeloma and for leukemia did not differ greatly. In men who started working before age 25, an excess was seen only for leukemia. There was no evidence for an excess of either category of cancer in men who started working after 1934.

Table 1. Observed and expected deaths due to selected diseases, according to work area in which employee usually worked

Disease	Work area	Number of deaths	
		Observed	Expected
All gastrointestinal cancer	Processing	52	38.2
	Rubber reclaim	11	7.7
Stomach cancer	Processing	18	9.9
Large intestine cancer	Processing	14	10.5
Pancreas cancer	Elevator/cleaning	6	2.9
Lung cancer	Tire curing	20	12.4
Prostate cancer	Miscellaneous tire	12	8.8
Bladder cancer	Warehouse/shipping	8	2.6
	Tire building	9	4.8
	All	48	39.5
Brain cancer	Tire building	7	3.7
Lymphatic cancer and myeloma	Tire building	11	7.1
Leukemia	Tires	18	11.7
	Processing	10	4.2
	All	55	43.0
Asthma	Services	11	7.0
Diabetes	Warehouse/shipping	11	5.8
Vascular diseases of central nervous system	Operating services	19	14.1
Pneumonia	Tire curing	12	7.7

Table 2. Standard mortality ratios (and observed deaths) for selected cancers, according to selected characteristics

Characteristic	Category	Gastro-intestinal cancer[a]	Lung cancer[b]	Bladder cancer[c]	Lymphatic cancer and myeloma[c]	Leukemia[c]
Age started working	<25	120 (7)	90 (4)	110 (7)	90 (14)	180 (19)
	25-34	120 (22)	220 (24)	130 (21)	110 (22)	100 (18)
	≥35	160 (23)	50 (3)	120 (20)	110 (15)	120 (18)
Year started working	<1925	130 (21)	130 (8)	140 (24)	100 (14)	140 (21)
	1925-34	130 (22)	200 (14)	140 (19)	120 (22)	160 (25)
	≥1935	180 (9)	120 (9)	60 (5)	80 (15)	70 (9)
Years worked	5-24	150 (24)	130 (11)	110 (17)	100 (24)	90 (18)
	25-34	140 (20)	140 (10)	100 (14)	90 (13)	170 (23)
	≥35	100 (8)	200 (10)	170 (17)	120 (14)	150 (14)
Age at death	<65	110 (18)	140 (17)	100 (14)	100 (29)	120 (25)
	65-74	110 (16)	140 (10)	90 (13)	100 (15)	150 (21)
	≥75	250 (18)	220 (4)	220 (21)	110 (7)	110 (9)
Year of death	<1955	110 (13)	70 (2)	90 (8)	130 (12)	120 (12)
	1955-64	160 (21)	160 (12)	130 (17)	90 (17)	150 (23)
	≥1965	130 (18)	160 (17)	130 (23)	100 (22)	110 (20)

[a] Employees who usually worked in processing.

[b] Employees who ever worked in tire curing.

[c] All employees.

The mortality studies have identified the plant areas and occupations, which require study to elucidate possible carcinogenic agents. Such studies obviously have the major shortcoming that a discontinued exposure could be responsible for some of today's mortality. One must deal with long induction periods in cancer, usually a minimum of 20 years in duration. The rubber industry has certainly been dynamic, and materials and processes have changed. However, based on these data and other confirming studies, we are attempting to identify specific substances that may be responsible for gastrointestinal cancer in processing workers, lung cancer in tire-curing workers, and bladder cancer and leukemia in general workers.

OCCUPATIONAL HEALTH FIELD STUDIES

Our field study program was initiated by a detailed walk-through survey of all plants covered by the "agreements" during 1971 and 1972 to gain familiarity with the materials and the processes involved in the manufacture of rubber products and the potential occupational health hazards. Our major management contact at each plant was the personnel manager, although we interviewed the plant manager, production personnel, safety staff, and medical staff. We contacted the local union president and met with union members of the safety committee.

Our interview with the company management prior to the plant survey was designed to develop information on safety and occupational disease statistics; broad personnel data such as population, turnover, and age distribution of factory workers; a management consensus of the important occupational health problems; and an outline of the plant medical coverage.

A meeting held with union personnel provided a list of the major industrial health concerns of the union membership, including specific plant problems and control difficulties. An early meeting with the union permitted us to view these specific areas during our plant tour.

A detailed preliminary industrial hygiene survey of the plant was conducted with both management and union representatives. The company representative was usually the staff person who had responsibility for safety, and the union member was either the local president or the chairman of the union safety committee. All production areas were visited. Detailed information was made available on materials, processes, and environmental controls. Our access to plant areas and to specific information on processes was complete in both companies.

A proposal was then prepared and submitted to the Occupational Health Committee identifying the companywide problems that we felt deserved either correction or further research. This approach led to the choice of a number of field studies, and I will briefly describe the results of three of these studies.

Curing Room Study

A medical study of workers in the curing rooms was completed in three plants of one company. The plants were selected based on the extent of the curing fume problem and on the stability of the work population. A concurrent industrial hygiene survey was conducted.

Since the specific causal agent was not known, the exposures of workers were characterized by personal air sampling for respirable mass particulate. This sampling program permitted us to define broad exposure classifications of all workers in this study.

Laboratory studies are now underway to define a specific sampling and analytical method for the principal agents.

The exposed population numbered about 200 workers in the study group, and a similar group of the same age and duration of employment not exposed to curing fumes was selected as the control population.

A questionnaire was administered at each of the plants to ascertain current symptoms, past medical history, lifetime occupational history, and smoking habits. Height and weight were determined. Posterior, anterior, and lateral X-rays were taken in full expansion to ascertain total lung capacity and evidence of X-ray abnormality. Pulmonary function testing included determinations of forced vital capacity (FVC) and forced expiratory volumes (FEV) on both populations.

From this study we were able to demonstrate that 25 percent of those curing room workers with greater than 10 years exposure have chronic obstructive lung disease. The increase in respiratory morbidity was related to both intensity and length of exposure to fume. The mean 1-year loss of $FEV_{1.0}$ in curing workers with greater than 10 years of exposure was significantly greater than the control groups and 3 to 5 times that due to aging. In addition, curing fumes produced an acute effect on the lungs; that is, during the day one could measure an effect from morning until night.

Processing Study

A similar study was conducted on 65 men exposed to dust in the processing area in three rubber tire-manufacturing plants. Compared to the controls, the processing workers had a higher prevalence of chronic productive cough, overall a decrease in the ratio of $FEV_{1.0}$ to FVC, and, in the group with greater than 10 years exposure, a significant decrease in the ratio of $FEV_{1.0}/FVC$, $FEV_{1.0}$, residual $FEV_{1.0}$, and flow rates at 50 and 25 percent of the forced vital capacity. These findings define obstructive lung disease in this population.

We have completed a preliminary air-sampling program in these processing areas. The respirable mass particulate concentrations range from 1-3 mg/m^3 with a significant portion of the respirable mass consisting of carbon black.

Industrial Talc Study

A population of 80 industrial talc workers at three tire-manufacturing plants has been studied by means of pulmonary function tests, chest X-rays, and respiratory questionnaires. The exposures of the workers were identified by both midget impinger and respirable mass-sampling techniques. The dust exposures were significantly below the present TLV of 20 MPPCF for nonfibrous talc with a quartz content of less than 0.5 percent. The workers did not demonstrate X-ray changes but did have evidence of respiratory morbidity. For each year of exposure to talc there was a 25-ml loss of $FEV_{1.0}$ in excess of that attributed to age and smoking.

LABORATORY INVESTIGATIONS

Dr. Avram Gold described work on the isolation of carcinogenic adsorbates on charcoal. This study will be later translated into specific field sampling and analytical methods to properly describe the exposure of workers in the processing area to carbon black. In another major laboratory study, Dr. Otto Grubner, a member of the Occupational Health Research Group at Harvard is conducting a detailed study of chemical compounds that become airborne during the curing of tires. Although this study is not concluded, preliminary comments on the investigative techniques and results can be made at this time.

A number of experiments involving different quantities of tire tread stock have been made. In one investigation the stock was cured in a special all-glass apparatus at a temperature of 150° C for approximately 70 hours. The chemical compounds evolved were collected in a freezing trap cooled to -78°C followed with a glass tube filled with 1.02 g of activated charcoal. Samples of the off-gases were analyzed by gas chromatography using a nonpolar column and a polar liquid phase column in parallel. The off-gases were analyzed at regular intervals by gas-chromatography and revealed that no organic substances in concentration detectible by the flame-ionization detector were passing through the charcoal bed. Samples taken from the inlet portion of the adsorption bed contained at least five organic compounds. The retention times of these compounds were different when analyzed by the two columns, with better separation obtained on the polar column. At least three of the organic compounds were identified as thiols of disulfides by reaction with N-N dimethyl-p-phenylenediamine. The Kovats's Indices of these peaks indicated that the compounds under consideration were probably propyl-thiol, butyl-thiol and methyl-butyl-thiol.

A fraction from the freezing trap was dissolved in precooled pentane, another in precooled methylene chloride, and samples of these solutions were analyzed by gas chromatography, using various combinations of columns with different liquid phases, subtractive chromatography, pretreatment of the samples with dinitrophenylhydrazine, molecular sieve 5A, and microscale reduction of the sample by hydrogen over a palladium catalyst. These experiments are summarized below.

A few aliquots of the sample gave a positive colorimetric reaction with N-N dimethyl-p-phenylenediamine, indicating the presence of thiols in the sample. It can be assumed that even higher homologues of thiols than those identified in the gaseous phase were contained in the sample.

Pretreatment of other aliquots of the sample with dinitrophenyl hydrazine did not give positive reaction for aldo or keto groups, indicating that aldehydes or ketones were probably not present in the sample. The gas chromatrographic spectrum of the sample remained unchanged when the sample was treated with molecular sieve 4A, indicating that normal paraffins and their derivatives were not present.

The catalytic reduction of sample aliquots did not change the gas chromatographic spectrum of the sample. This suggests that no easily reducible compounds were present in the sample. The very low concentration of the organic compounds in the sample as well as the relatively short time of reduction (2 hours) may have limited the reduction.

Subtractive gas chromatography employing a short silica gel column saturated with sulphuric acid inserted between the regular column and the detector, as well as the evaluation of gas chromatograph spectra obtained on SE 52, Carbowax 20 M and polypropylene-glycol-silver columns, made it possible to tentatively identify the nature of some of the 35 compounds found in the sample. Some were classified as olefins, others as iso-paraffins, and others as aromatic compounds. The aromatic compounds were predominant.

The total yield of products gained in the process of curing 62.8 g of the tire substrate was at least 20 mg, with 10 mg adsorbed on the charcoal adsorption tube. Compounds adsorbed on the charcoal have not been analyzed.

With completion of this work, we will hopefully identify the critical compounds of the curing off-gases, and based on that identification we will design our in-plant sampling system to describe adequately the workers' exposure.

In my introduction, I indicated that our program was interdisciplinary, with physicians, epidemiologists, industrial hygienists, chemists, and physicists working together to identify hazards and control them. I believe the descriptions of the North Carolina and Harvard programs indicate the success of this Joint URW-company-university program.

ACKNOWLEDGMENT

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DISCUSSION

MR. HARRY J. COLLYER (Cabot Corporation, Billerica, Mass.): Mr. Burgess, was Dr. Avran Gold's work done on adsorbates, from charcoal, or on carbon black?

MR. BURGESS: On carbon black.

MR. LOUIS S. BELICZKY (United Rubber Workers International Union, Akron, Ohio): I am sure Dr. Gold's comments generated interest during the session. We have been aware of some of his findings and I think Dr. Gold approached the problem very academically. It is interesting to note that another research organization essentially came up with the same kind of results involved.

Former information presented a year or so ago raised quite a few eyebrows when someone said that he found benzopyrene in carbon black. I have been in plants where I have walked in three, four, or five inches of carbon black and it has taken me days to get the carbon black from my skin and my clothing.

The real concern is that the threshold limit value for carbon black, which is 3.5 mg per cubic meter, has been assigned by chance. This resulted when the American Conference of Governmental Industrial Hygienists asked a gentleman by the name of Sands, formerly of the Uniroyal Corporation, what he thought the control level of carbon black concentration in the worker's breathing zone could be. He thought for a while and said, "Well, I think that the proper engineering control level that we can achieve at this time is 3.5 mg per cubic meter of air. The basis for the establishment of the threshold limit value for carbon black was an estimate based on the ability of a ventilation system to reduce worker exposure to carbon black. We must now seriously look at this threshold limit value, when we consider that four carcinogens have been isolated on carbon black and that perhaps we may consider the carbon entity as a potential carcinogen, per se.

MR. GEORGE L. WILSON (Local 17 of United Rubber Workers Union, The B. F. Goodrich Tire and Rubber Company, Akron, Ohio): Professor Burgess, I understood you to say that appropriate threshold limit values of talc might either be .25 or .5 mg per cubic meter. Can you comment a little further on that? Have you decided which one might be appropriate?

MR. BURGESS: We have not made a decision on an appropriate TLV for industrial talc. The concentration one chooses depends on the penalty in FEV 1.0 one is willing to accept.

CHAIRMAN BELICZKY: Dr. Longley?

DR. MARS Y. LONGLEY (Sohio, Cleveland, Ohio): Along those lines, how long back in time did you suppose the level of quartz in talc was under .5 percent?

MR. BURGESS: In the particular company we were working with, it was at least a decade, and possibly longer.

MR. WILSON: Regarding the manual versus the automatic tire press--heavy versus light industrial--is there any difference in the tire compound?

MR. BURGESS: There are differences in compounds; however, we were not able to resolve the exposure to that degree.

MR. BELICZKY: We are concerned with the common dusts used as lubricating materials in the rubber industry. Talc is a mineral in general use and our concern is three-fold: (1) talc, per se, produces TALCOSIS, without considering, (2) the free-silica content in concentrations above 1 percent and more significantly, that (3) asbestos fiber may be found in talc. Asbestos is well known for its production of lung as well as mesotheliomal cancer.

The term "soapstone" in the industry usually includes the mineral, per we, and also is used to include clay, mica, talc, and even zinc stearate. All four have been implicated in pulmonary fibrosis. Clay and mica may produce pneumoconiosis because of the free crystalline silica contained in them. Talc may contain asbestos fibers as well as free silica. The data generated from the university programs should lead to control by "controlled-purchasing," i.e., by only purchasing materials containing less that 1 percent free crystalline silica and no asbestos fibers. The same philosophy shall be applied to the purchase of petroleum distillates, including hexane, gasoline, petroleum, and similar napthas: they shall contain less than 1 percent benzene, and be purchased accordingly. Benzene is a carcinogen.

The amorphous silicas are also of concern, and they and the other pneumoconiosis producing dusts mentioned above must be handled with proper engineering and environmental control.

Professor Burgess referred to heat and environmental heat stress problems. I served on the DOL's Heat Stress Advisory Committee, which completed its deliberation in November, 1973. The committee's recommendations were sent to the Assistant Secretary of Labor, who forwarded them to the National Institute for Occupational Safety and Health on April 11, 1974. On April 13, 1974, the director of NIOSH returned then to OSHA, and the recommended document sits there today--just gathering dust.

OSHA's excuse for this delay in promulgating a standard is based on lack of adequate documentation to justify a standard--"Not enough workers are dying or being seriously injured by environmentally induced heat stress or heat strain." Only prejudiced management data was included in the committee meetings--organized labor had minimal mortality or morbidity data to sway the Office of the Assistant Secretary of Labor. Both Harvard and the University of North Carolina are studying environmental heat stress, and hopefully their data will point to the development of a standard which will adequately protect workers from the adverse effect of heat stress.

CONFERENCE SUMMATION

Farley Fisher

GENERAL CHAIRMAN FISHER: Our plan at this point is to give each of the session chairmen 5 to 10 minutes to comment on his session or on the rest of the conference. Unfortunately, two of our session chairmen are not with us today because of other commitments. Mr. Robert C. Niles of Uniroyal, Inc., Chairman of Session I, had planned to be here but unfortunately could not. Mr. David Garrett of the Office of Toxic Substances at EPA in Washington was to substitute for Mr. Niles, but he too was unable to attend today. However, Session I was very informative, especially concerning the techniques for controlling odor problems and effluent problems.

Mr. William E. McCormick of the American Industrial Hygiene Association was also unable to be here today, and I have asked Dr. George Levinskas to substitute for him at this time. Dr. Levinskas is eminently qualified to serve in place of Mr. McCormick. He is an industrial hygienist with experience in occupational health, and currently holds the position of Manager of Enivronmental Assessment and Toxicology for the Monsanto Corporation.

DR. GEORGE J. LEVINSKAS (Monsanto Corporation, St. Louis, Mo.): The sessions have ranged quite widely from experimental toxicity tests on animals, to clinical observations of human health, to chemical and physical studies measuring various parameters dealing with some phase of making or using rubber.

One of the speakers made a passing reference implying that animal toxicity data had no relationship to and limited value for the assessment of the effects of chemicals on man. I must take strong exception to that remark. Test data obtained by exposing animals to chemicals are useful in predicting their probable effects on man. There may be many difficulties in evaluating the low incidence of a given finding in animals. This is a situation comparable to the difficulties an analyst has in detecting a peak in a tracing when it is not much above the background noise generated by his instrument. There may be uncertainties as to the relative susceptibility of man versus the animals for a given material. There are many other problems in evaluating

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potential risk to man from exposure to a given substance as judged by animal studies. However, despite the real and sometimes imagined drawbacks to animal tests, these tests have been, are now, and will continue to be useful in evaluating the health effects of chemical substances on man.

Several of the papers point up the need for the measurement of materials, qualitatively and quantitatively, in the environment. We need to know what, and how much, is out there before we can begin to assess the potential hazards to man or to the environment of these various materials. However, because of today's technology, chemists have exceedingly powerful analytical tools at their disposal. We should remember that, while discovery of a new contaminant raises a question as to its significance, it does not necessarily portend doom and gloom. In fact, under different conditions, a similar situation may be either bad or good. A used tire dumped in a lake or settled on the bottom of a swimming hole represents undesirable litter. The same tire sunk in an estuary becomes a beneficial, artificial reef. The reason we judge one situation to be bad, and the other to be good, is based either on our personal experience or on our prior conditioning to accept a belief.

It has been remarked at this conference that researchers do not like to publish negative data, i.e., data supporting safety. Researchers prefer to publish findings. I have no quarrel with that view. However, we should be attempting to define those areas in which there could be a high probability of risk. This requires objective reporting of data. The use of overtones and innuendos to imply that imminent disaster is coupled with every finding of a new environmental contaminant, no matter how small its concentration may be, is misleading. It can only confuse the litter tire and the reef tire.

MR. J. R. LAMAN (The Firestone Tire and Rubber Company, Akron, Ohio): Our group in environmental engineering and I are sure that other environmental engineering groups in major corporations are consistently seeking to strengthen the interface with toxicology, industrial medicine, and industrial hygiene. I feel that a major item for consideration was left out of this conference; namely, no one talked about the double line. Unfortunately, the double line must be considered because it reduces to profitability and/or economics. There is no free lunch counter in this business. Unfortunately, no attempts were made to equate cost/benefit/risk with quality of life, or lifestyle. When we talk about this lunch counter business, it involves everybody. Somebody has got to pay the costs.

My field is strictly the engineering approach; for example, in a water problem, we get down to specified levels and then make an ecological judgment of the system. We fine-tune as required. We strike a good cost/benefit/safety balance. We must never forget that our pollution control approach must be tuned to the highly developed nations, which are competing for our markets and services. The highly developed nations must embrace pollution control as a cost of doing business, as we are doing, to compete fairly. By juggling the equation, some component of the equation will be affected.

Let me repeat it again: cost/benefit/risk equals quality of life, or lifestyle.

Since we have the highest standard of living that humanity has known, we must prudently chart our course; because if we do not, it will be unfairly taken off the top.

The environmental engineers in this very worthwhile conference offered to us many pollution-free ways of disposing of tires. Tires can be properly disposed of in incinerator boilers, fish reefs, and conventional reclaim.

At this time, we should look at the economical feasibility of all the disposal technologies just discussed as well as other technologies just emerging, which are described in the literature. By balancing the cost/benefit/risk ratio with economics, I am sure that we can find a suitable solution for the disposal of these tires without adversely affecting the ecosystem. In conclusion, we must determine who is going to pay the price.

GENERAL CHAIRMAN FISHER: Mr. Beliczky, do you have some more remarks?

MR. LOUIS S. BELICZKY (United Rubber Workers International Union, Akron, Ohio): All of us know our moral and social responsibility in the area of air pollution. Organized labor's role in air pollution problems has been minimal to date. We have probably been more concerned about the workers' in-plant environmental health problems than about out-plant emissions.

We must have an awareness of the serious hazards from air and water effluents to the population in general. A few months ago a news release implicated increased birth malformations to areas along Lake Erie where polyvinyl chloride resin manufacturing plants were located: Avon Lake, Painesville, and Astabula.

EPA reports conducted in 1974 indicated that vinyl chloride was found by air and stream emission studies in the areas implicated. No real scientific studies to date have directly implicated vinly chloride to the increased incidence of birth malformations. Before positive judgments are made, more objective studies must be conducted, keeping in mind that at each site mentioned, power-generating plants have been also operating for many years.

We must be concerned that four carcinogens have been identified as being present in the carbon black actually used in the rubber industry. The fact that we are beginning to identify some of the chemicals being produced in rubber curing processes must be emphasized. Dr. Rappaport's presentation and studies being conducted by Harvard may lead us to an identification of specific causative factors producing the many forms of cancer which were mentioned by Dr. Harris and Professor Burgess.

Greater emphasis must be placed on morbidity studies so necessary to follow up on the mortality (epidemiological) data. Only through joint and concerted investigations can we hope to successfully control the hazards to which our workers are exposed. The workers themselves negotiated the $10.20 per year that is set aside for the university studies.

Each segment of specialized studies will eventually lead to that safe and healthful work environment to which each working man and women is entitled. Perhaps the data will assist in controlling the whole system--his environmental health at work and away from the job.

I must respond to the statement of relating animal toxicity data to human beings. I can only state that if a material has been proven to be carcinogenic to animals, but no data are available to document it as a causative agent in producing human cancer, it cannot be dismissed as being safe for human beings.

This philosophy has been capriously applied to vinyl chloride and to 2, 4, methylene-bis-2-chloroaniline (MOCA) by those who hold the dollars and cents of profit over lives.

Indiscriminate judgments regarding workers' health are sometimes made by the uninformed and callous decisionmakers. Who really pays? It is mainly the workers who pay from their pockets and/or with their health or lives.

DR. FISHER: The questions are: What are the problems, and where can we take these problems to make progress? We are limited; we are merely mortals and we cannot do everything at the same time.

What are the areas we have to move into first to identify and then control those things that are the greatest threat to our health and our environment? These are the kind of things I think we are trying to get at here, as they concern all of us. At the same time, it is important not to get so hung up with talking about what we were going to do that we do not actually make progress.

I hope that having this meeting and these discussions has stimulated people to think in the areas where they had perhaps not thought before, because of ignorance, not because of intent. I hope you all learned something; I know I have certainly learned a lot here from all of you and I appreciate it very much.

Submitted Papers--
Not Presented at Conference

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TOXICOLOGY AND PHYSIOLOGICAL EFFECTS OF PHILLIPS OIL FURNACE CARBON BLACKS

Lucian E. Renes*

Abstract

The paper discusses the composition of the adsorbed polycyclic aromatic hydrocarbons on Phillips present day oil-furnace carbon blacks, and describes briefly the various toxicological studies with whole carbon blacks, and with a known carcinogen that did not induce any neoplastic changes after long-term exposure. These studies support the absence of any physiological effects among carbon black workers with 20 or more years of exposure.

In December 1943, Phillips Petroleum Company began operation of a plant in Borger, Texas, designed to manufacture furnace type carbon blacks from liquid hydrocarbons. The process was based upon a newly developed tangential reactor which utilized a feed stock of aromatic rich oil and produced carbon blacks of selected physical and chemical properties and of uniform quality. Most oil furnace blacks used in the rubber industry are produced by this form of reactor.

Very early in the operation of the plant, the employees accepted the use of special work clothing and barrier creams to minimize discoloring of their skin and to avoid soiling of their street clothing. clean work clothing, including long underwear, coveralls, sox, and canvas shoes were provided daily by the company. Shower facilities, soap, and towels were also furnished to facilitate cleansing of the skin at the end of the work shift.

Periodic medical examinations were initiated on all Phillips' employees in the Borger area in 1949, and in the case of the carbon black workers their examinations included a chest X-ray every 2 years. Pulmonary function tests were initiated on all carbon black workers in 1959. These medical examinations have been continued to date. Early this year, the medical records of about 135 employees

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*Director, Industrial Hygiene and Toxicology, Medical Division, Phillips Petroleum Company, Bartlesville, Oklahoma 74004.

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with 20 or more years experience in the company's carbon black operations in Borger were reviewed by a member of Phillips' medical staff. In his opinion, the records revealed the absence of any specific health effects attributable to working in carbon black. Cases of dermatologic problems including skin cancers were few in number, and cases of pulmonary related problems including carcinoma of the lung were also few. Based entirely on the medical records of this group of carbon black workers, it appears that their overall health is superior to that of a comparable general male population. Further, the overall mortality, as well as the mortality from any specific cause, appears to be below that of a comparable population group.

During the period 1949-1971, Phillips and six other carbon black producers sponsored a program of research under the direction of Carl A. Nau to determine the physiological response of experimental animals to carbon black by various routes of exposure. The results of this research program were published in a series of five reports in the AMA Archives of Industrial Health between the years 1957-1962. Although these carbon blacks were known to contain small amounts of adsorbed 3,4-benzpyrene, this research demonstrated unequivocally that 50-percent lifetime or longer exposure of experimental animals to whole carbon blacks did not produce any malignancies or other harmful effects as a result of ingestion, skin contact, or inhalation of the whole carbon black.

In 1965, the American Petroleum Institute sponsored a research project to determine the dose-response relationship of the carcinogen, 3,4-benzpyrene in the pulmonary tract of experimental animals (ref. 4). The work was performed at the Chicago Medical School under the direction of Dr. Phillippe Shubik, presently director of the Eppley Institute for Research in Cancer. It was found that the highest dose of 3,4-benzpyrene adsorbed on a carrier dust, administered once a week for 30 consecutive weeks, which did not induce any neoplastic changes was 0.5 mg per animal. This dosage is about 1,000 times the quantity of 3,4-benzpyrene, which could be inhaled daily by a worker exposed to the present day threshold limit value of carbon blacks containing as much as 10 ppm by weight of this compound.

Several years ago, in response to the needs of the rubber industry, Phillips had developed a series of new blacks whose particle porosity was lower and whose adsorbed residual oils were slightly higher than the furnace blacks previously manufactured. For this reason, the company considered it of interest to determine the analytical composition of the adsorbed materials in the new blacks. Prior to 1970, the qualitative and quantitative composition of the materials adsorbed on the carbon black particles was not accurately defined. It had been shown by a few early investigators that representatives of several classes of polycyclic aromatic hydrocarbons were among the materials adsorbed on the carbon black. Among this group, the hydrocarbon 3,4-benzpyrene, a compound of proven carcinogenic properties in experimental animals, had been shown to be present in minute amounts. Since the chromatographic techniques required to resolve a mixture of polycyclic aromatic hydrocarbons into separate individual components had not reached a high state of refinement until recent years, the accuracy of older measurements of certain compounds, such as 3,4-benzpyrene, has been questioned because of interfering impurities. No systematic treatment is equally successful for different mixtures of these hydrocarbons. However, certain laboratories, such as that of the Eppley Institute for Research in Cancer, have developed great skills in the analyses of materials containing polycyclic aromatic constituents.

The analytical laboratories of the Eppley Institute for Research in Cancer, University of Nebraska Medical Center, were selected to make such analyses because of their extensive experience in studying the composition and carcinogenicity of such materials as petroleum waxes, petroleum asphalts, coal tar products, and other substances of pyrolytic origin. For the interest of those persons who are not familiar with Eppley Institute, its director, Dr. Phillippe Shubik, is world renowned for his contributions to the study and knowledge of chemical carcinogens. The professional staff of the Institute are persons of great skills and experience in the medical and chemical sciences utilized in cancer research.

Ten different carbon black samples of present day manufacture, representing different feed stocks, different particle size range, and different amounts of adsorbed residual oils, were submitted to Eppley Institute for analysis. The adsorbed materials were extracted in the absence of light with refluxing benzene in a Sohxlet apparatus for 48 hours. This procedure has been demonstrated to extract the maximum amount of adsorbed materials that can be removed from carbon blacks by any known means. The mixture of materials was resolved into individual compounds by a systematic procedure of thin layer chromatography on alumina and then on acetylated cellulose plates. Gas liquid chromatography was also utilized when required. The separated components prepared for uv-vis spectroscopy were examined in a Cary 14 spectometer or a Beckman DB-GT, as required. Duplicate analyses were made on each carbon black.

At the company's request, Eppley Institute determined quantitatively every major polycyclic aromatic hydrocarbon present in the material extracted from each carbon black. Analytically, the results of the examination were astonishing. Such common substances as anthracene and chrysene were absent in the list of polycyclic aromatic hydrocarbons identified. Further, there were no methyl derivatives of any of the polycyclics determined in contrast to the large number of methyl derivatives found in coal tar distillates. Of most importance, the only compound of proven experimental carcinogenicity found in the carbon blacks was 3,4-benzpyrene. The concentration of this substance in the commercial blacks ranged from 0.8-6.7 ppm by weight. Other carcinogenic compounds such as 1,2,5,6-dibenzanthracene, 9,10-dimethyl benzanthracene and 1,2-benzanthracene were absent. One specific commercial black was entirely devoid of any proven carcinogen including 3,4-benzpyrene. Since the analytical procedures were capable of detecting these particular compounds to a lower limit of 10 parts per billion by weight, we consider this level of absence comparable to a "philosophical zero."

In analyzing this family of carbon blacks, Eppley Institute (ref. 1) isolated and measured a nonfluorescent, polycyclic hydrocarbon identified as cyclopenta(cd)pyrene. It is of experimental interest because it is the first known cyclo alkenyl pyrene derivative that appears in such common materials as gasoline exhaust particulates, incinerator soots, coal tar pitch, and general atmospheric soot. A few years ago, researchers (ref. 2) at the Texas University Medical School, Galveston Branch, had isolated this material from various materials including carbon blacks. Bio-assays of this isolate were performed by injecting known quantities of the material, dissolved in cooking oil, subcutaneously in mice. Eight of 16 mice developed fibrosarcomas at the site of injection after 244 days at a dose of 6.5 mg of isolate per mouse.

The selection of appropriate animal species and methods of application for carcinogenicity testing have been discussed by various cancer researchers (ref. 3). Using such views as a basis of judgment, it is not reasonable to ascribe any greater significance than presumptive carcinogenicity to the bio-assay results on cyclopenta(cd)pyrene. But whether or not this particular compound is carcinogenic does not alter the findings of Dr Carl Nau's extensive research, that whole carbon blacks are harmless to experimental animals. Of greater importance is the fact that the medical study of workers with 20 or more years of exposure to carbon black does not show any harmful effects attributable to carbon blacks.

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AN ECONOMIC EVALUATION OF THE USE OF CRYOGENICS IN RUBBER TIRE RECLAIMING

S. L. Fredericks*

Abstract

Discarded rubber tires represent 7 percent of the total solid waste disposal in the United States. This is 5 billion pounds of potentially reusable materials. Less than one-third of all discarded tires are reclaimed. An economical way of reclaiming old tires, including steel-belted radials, is through a cryogenic system. A liquid nitrogen tunnel coupled with a tire shredder and a hammer mill will produce satisfactory crumb rubber. This paper describes such a system.

PREFACE

The American people suddenly realize that the world's natural resources are no longer infinite and that we must conserve. America represents 8 percent of the world's population, and we consume over 40 percent of the world's yearly production. The rest of the world is starting to catch up, and there just isn't enough of everything to go around anymore. Consequently, we Americans must learn to conserve and recycle our planned-obsolescence materials. Automobile tires, a byproduct of petroleum, are one important solid waste that we must recycle.

BACKGROUND

The many restrictions on the use of landfills for solid waste disposal have affected the solid waste disposal industry very severely. Tires represent 7 percent of total solid waste material in this country. In years gone by, it was common practice to discard old tires in the local dump. This is no longer permitted, as tires are not biodegradable and have a tendency to "wiggle" to the surface of the land-fill. If tires are cut into quarter sections, they are acceptable, but this costs money to do.

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*Manager, Process Sales, Airco Industrial Gases, 575 Mountain Avenue, Murray Hill, New Jersey 07974.

Disposal by conventional burning is no longer acceptable because of air pollution; however, some efforts have developed EPA-acceptable prototype tire incinerators.

Some tires have been used for making artificial fishing reefs. However, unless the tires are filled with concrete before assembly in the water, they will eventually work free from their metal straps and float to the surface. This has already happened in San Francisco Bay. If the tires must be filled with concrete, this is an expensive way of discarding them. It is more practical and economical to recycle the rubber.

Approximately 250 million tires are manufactured each year, and they end up on the trash heap at about that rate; about one tire for each American. It is also estimated that about 2 billion tires are, at present, discarded and waiting for disposal.

Some tires can be retreaded and reused. Retreading the tire does not solve the disposal problem as the retreaded tire soon ends up as a solid waste disposal problem.

Several companies now reclaim about 30 percent of the tires produced (about 80 million tires per year). These reclaimers also process rubber factory scrap, tire buffings, and inner tubes.

The price of natural rubber on the New York Commodities Exchange on December 9, 1974, was $0.41/lb with promised delivery for March 1975. In December of 1973, the average price of natural rubber was $0.54/lb. At present, the demand is down, and there is very little trading. The price of synthetic rubber has doubled in the past 2 years from $0.16/lb to over $0.30/lb. The supply of synthetic rubber is not tight except for neoprene. Synthetic rubber prices increased because of increase in raw-material costs (crude oil and its derivatives) and the rising cost of energy.

Petroleum companies once sold their byproducts to rubber producers at an extremely low price as a means of disposing of them. As the demand increased for these byproducts, the price has increased.

The price of reclaimed devulcanized rubber was frozen at $0.105/lb under price controls, but the present average price is $0.14/lb. The selling price of crumb rubber is from $0.08 to $0.10/lb. This economic survey is based on these two selling prices.

The production of reclaimed rubber has dropped from 300,000 tons a year in 1950 to its present low figure of approximately 170,000 tons per year. The primary cause is the large initial investment required to build a tire reclaimer and a recent decision by major tire manufacturers to shut down their extensive reclaim systems because of rising costs and, particularly, because of EPA requirements on smoke abatement. The "devulcanizer" system requires an expensive pollution-control system.

The reclaiming process involves the separation of fabric and steel wire from the rubber. In most cases, the rubber is then disgested or depolymerized and blended with reclaiming oils. This material then can be recycled into tire manufacture and tire retreading; into making materials such as rubber hose, sink mats, floor mats, athletic running tracks; and into repairing asphalt roads, etc.

Very few products produced commercially use the rubber "as ground" for reuse in manufacture. Practically all reclaimed rubber ends up competing with new rubber. If processed crumb rubber is to be commercially feasible, then end uses that require little or no refining or reprocessing must be found for the ground rubber.

PRESENT-DAY RECYCLING PROCESS

The systems presently employed by most conventional tire reclaimers include tire slitters, tire cutters, and tire shredders. All of these ponderous units employ cutting equipment requiring frequent repair and servicing. It is estimated that the present conventional equipment and buildings required for processing 10 tons per hour of reclaimed crumb rubber from 30 mesh on down would cost approximately 3 million dollars.

Scrap rubber, including discarded tires, can be easily reclaimed by a cryogenic system. Cryogenic systems also separate and reclaim the wire and fiber, which have a ready resale market. The reclaimed rubber with its retained carbon black and oils is about 70 percent of the total tire weight (15/lb of a standard 20/lb tire), and the rest of the material is the wire and fibers.

One of the problems facing tire reclaimers today is the presence of the steel-belted radial tires. The conventional shredder system does not cleanly remove the belt wire mesh. As the tire is cut and shredded, the belt wires remain with the rubber pieces down to and including mesh size. It is almost impossible to remove the wire. At present, tire reclaimers do not accept steel-belted tires for reprocessing. The cryogenic system does not have this problem, since the frozen, brittle rubber is easily separated from the wire and fibers in a hammer mill.

Preliminary estimates have been made of a plant and process for recovering the rubber and other constituent materials from used tires. The rubber is recovered in the form of a ground powder (-30 mesh). Other recovered materials are fiber from the tire fabric, steel from the tire beads, and, in radial tires, steel from the reinforcing belts. The average tire is presumed to contain:

70 percent recoverable rubber;
15 percent fiber;
15 percent metal.

The following cost of estimates are based on preliminary information obtained from extensive field tests. Further process development may lead to some changes in the details of the process and plant. Such changes would not be expected to add significantly to the capital required or to the process complexity. The process diagram is shown in figure 1, and a possible plant layout in figure 2. Rated to dispose of a nominal 10 tons of tires per hour, the plant is expected to process 200 tons of tires per 24 hours of plant time.

CRYOGENIC PROCESS AND EQUIPMENT

The tires are loaded, using a crane and grab, into an overhead bin, which feeds a preshredder. The preshredder cuts the tires into chips of approximately 2 inches square, which fall onto a conveyor belt. The belt carries the chips up to the particle hopper from which they are fed at a constant rate onto a conveyor contained in a tunnel cooled by liquid nitrogen (fig. 3). The liquid nitrogen consumption is .8 lb per pound of chips cooled.

The now frozen chips are hard, rigid, and brittle. On leaving the tunnel they fall into a hammer mill, which shatters the rubber,

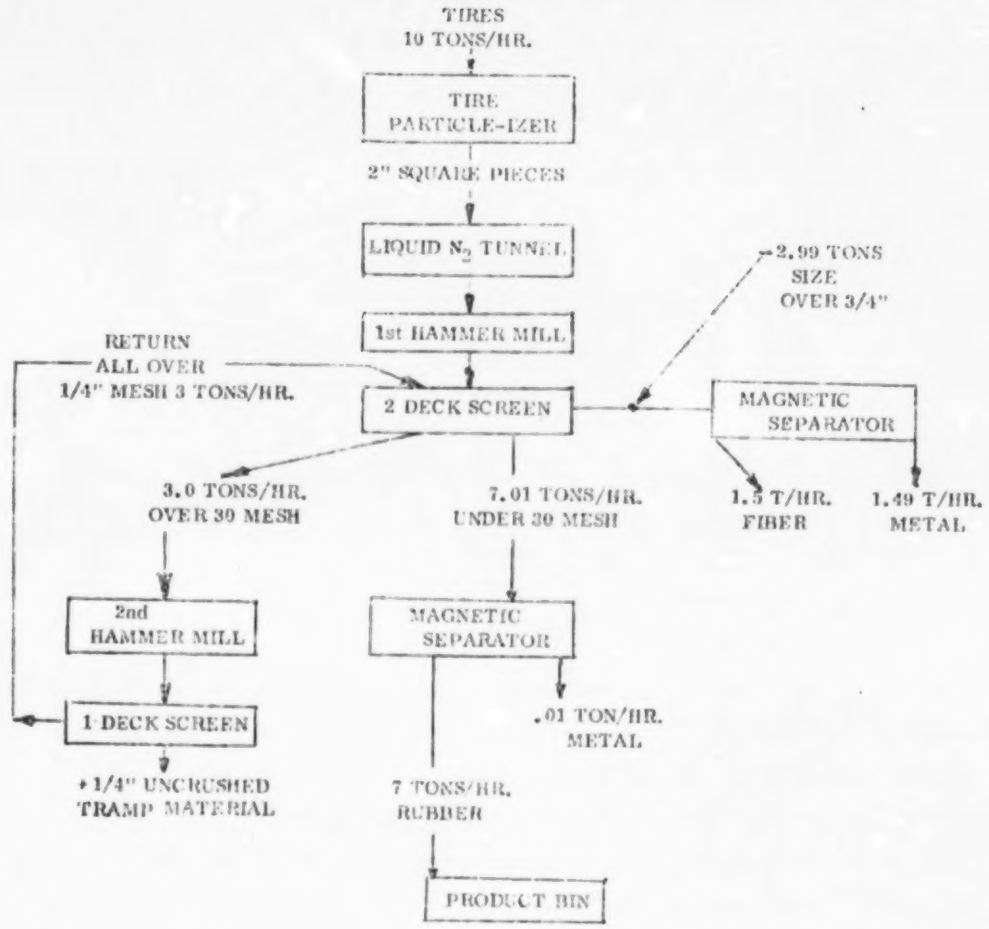
TIRES
10 TONS/HR.
TIRE PARTICLE-IZER
2" SQUARE PIECES
LIQUID N2 TUNNEL
1st HAMMER MILL
RETURN ALL OVER 1/4" MESH 3 TONS/HR.
2.99 TONS SIZE OVER 3/4"
2 DECK SCREEN
MAGNETIC SEPARATOR
3.0 TONS/HR. OVER 30 MESH
7.01 TONS/HR. UNDER 30 MESH
1.5 T/HR. FIBER
1.49 T/HR. METAL
2nd HAMMER MILL
MAGNETIC SEPARATOR
1 DECK SCREEN
.01 TON/HR. METAL
+1/4" UNCRUSHED TRAMP MATERIAL
7 TONS/HR. RUBBER
PRODUCT BIN

Figure 1. Process diagram: rubber recovery from tires.

separating it from the fabric and wire, and grinds the major portion of the rubber to less than 20 mesh.

A two-deck vibrating screen placed below the mill receives the discharged material. The uppermost screen mesh is selected to retain most of the fiber and wire, which remains nearer to the 2-in. chip size. This mixed fiber and wire is discharged onto a conveyor belt for further separation. The lower screen is 30 mesh; it separates the less-than-30-mesh rubber from the oversize rubber retained on the screen. The 30-mesh-and-under rubber is taken by conveyor and elevator to the product bin (rubber bin in figure 2). During its passage, metal fines that may

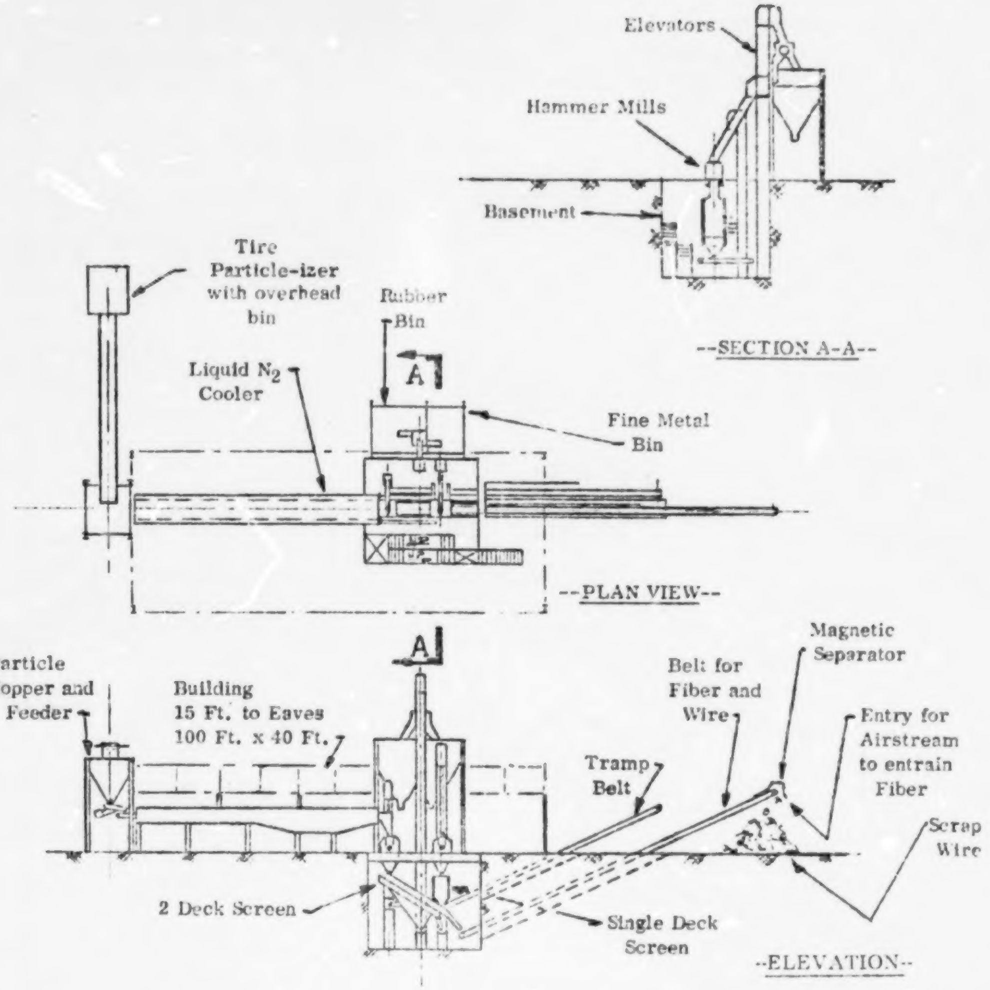
Elevators
Hammer Mills
Basement
--SECTION A-A--
Tire Particle-izer with overhead bin
Rubber Bin
Liquid N_2 Cooler
A
Fine Metal Bin
--PLAN VIEW--
A
Particle Hopper and Feeder
Building 15 Ft. to Eaves 100 Ft. x 40 Ft.
Belt for Fiber and Wire
Magnetic Separator
Entry for Airstream to entrain Fiber
Tramp Belt
Scrap Wire
2 Deck Screen
Single Deck Screen
--ELEVATION--

Figure 2. Preliminary layout of plant reclaiming rubber from tires.

have passed the 30-mesh screen are separated by a magnetic separator into an adjoining bin.

The oversize rubber, which is retained on the 30-mesh screen is discharged onto a conveyor and transferred via an elevator to a second hammer mill, where it is further reduced in size. This mill discharges onto a simple coarse screen, which separates out any tramp material that has not been shattered in the hammer mills. The material passing the screen is returned via conveyor and elevator to the entry of the first hammer mill and is thus recirculated. An allowance has been made in the

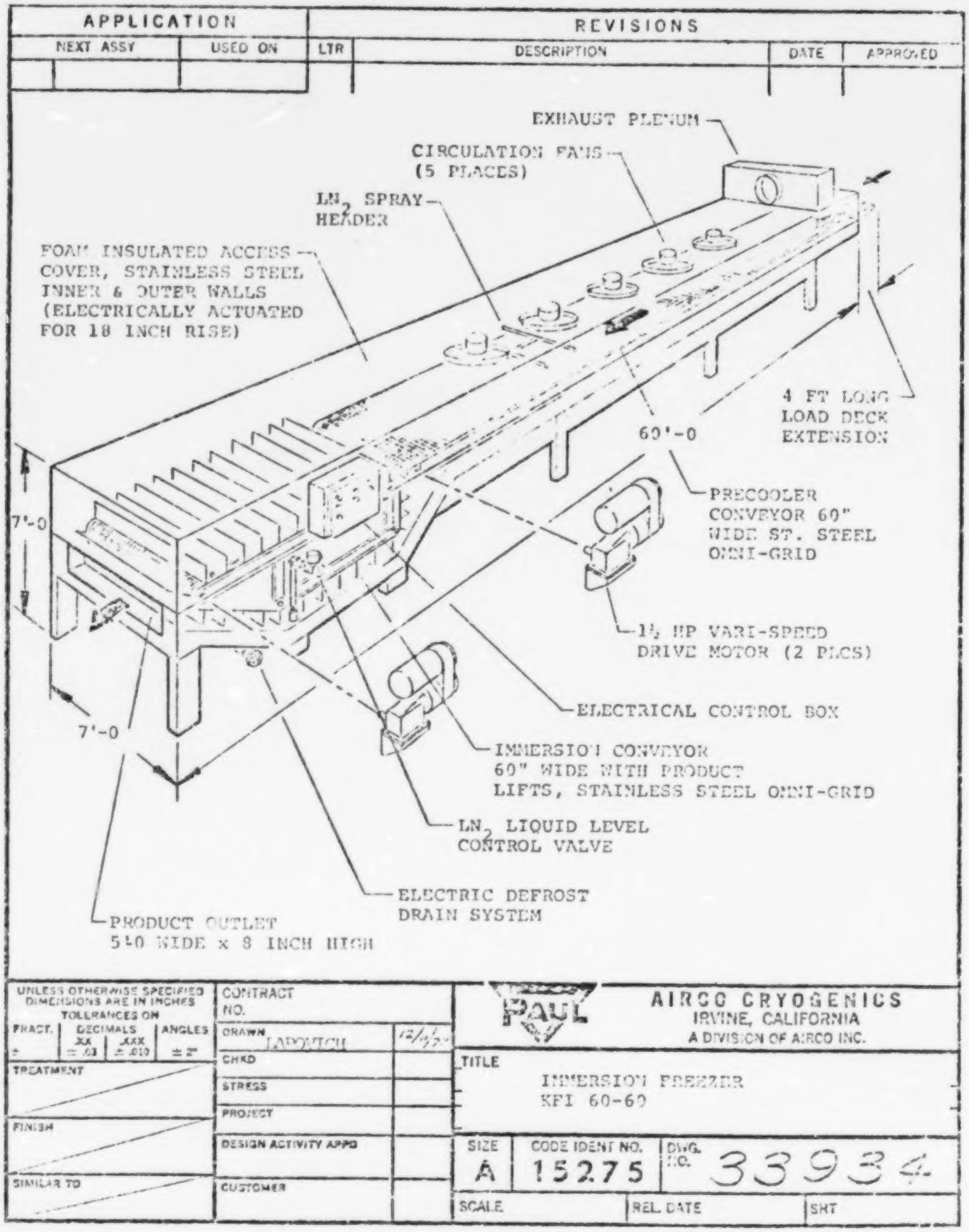
APPLICATION
NEXT ASSY
USED ON
REVISIONS
LTR
DESCRIPTION
DATE
APPROVED
EXHAUST PLENUM
CIRCULATION FANS (5 PLACES)
LN2 SPRAY HEADER
FOAM INSULATED ACCESS COVER, STAINLESS STEEL INNER & OUTER WALLS (ELECTRICALLY ACTUATED FOR 18 INCH RISE)
4 FT LONG LOAD DECK EXTENSION
60'-0
7'-0
PRECOOLER CONVEYOR 60" WIDE ST. STEEL OMNI-GRID
1½ HP VARI-SPEED DRIVE MOTOR (2 PLCS)
ELECTRICAL CONTROL BOX
7'-0
IMMERSION CONVEYOR 60" WIDE WITH PRODUCT LIFTS, STAINLESS STEEL OMNI-GRID
LN2 LIQUID LEVEL CONTROL VALVE
ELECTRIC DEFROST DRAIN SYSTEM
PRODUCT OUTLET 5'-0 WIDE x 8 INCH HIGH
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES ON
FRACT. ±
DECIMALS .XX ± .03
.XXX ± .010
ANGLES ± 2°
TREATMENT
FINISH
SIMILAR TO
CONTRACT NO.
DRAWN LADOVICH
CHKD
STRESS
PROJECT
DESIGN ACTIVITY APPD
CUSTOMER
PAUL
AIRCO CRYOGENICS
IRVINE, CALIFORNIA
A DIVISION OF AIRCO INC.
TITLE
IMMERSION FREEZER
KFI 60-60
SIZE A
CODE IDENT NO. 15275
DWG. NO. 33934
SCALE
REL. DATE
SHT

Figure 3. Proposal drawing.

estimate for insulation of the surfaces of equipment handling the cold material as it passes through the two hammer mills.

The conveyor belt carrying the mixed fiber and wire terminates in a magnetic section in order to separate fiber from the magnetic wire. In this section a magnetic pulley retains the wire while the fiber, being nonmagnetic, is removed by a rapid stream of air. Fiber is separated from this air stream by the use of cyclones (not shown in figure 2), and the scrap wire is discharged from the end of the belt.

MANPOWER

One foreman and five operators are required for running the plant, in addition to administrative personnel and a maintenance crew. When working on a continuous-week basis (7 days × 24 hours), there will be four shift crews. Each man will work 2,000 hours per year plus 160 hours overtime at time and a half.

RAW MATERIALS

The tires are assumed to be free of cost. (Calculations have also been made for the manufacturing costs when tires cost $25.00 per ton and when a premium is paid to the processor for tire disposal of $25.00 per ton.)

The cost of liquid nitrogen is taken to be $0.037/lb.

ESTIMATED INVESTED CAPITAL

This totals $881,000 and is shown in detail in table 1.

The investment includes a building 100 ft × 40 ft with basement, together with installed equipment on an assumed precleared site. A paved area of 1,000 yd^2 is allowed for.

The costs indicated in table 2 include a provision for 10 years straight-line depreciation.

Table 3 shows the effect on manufactured cost of varying the following:

1. cost of tires;
2. cost of liquid N_2;
3. level of production.

Table 1. Preliminary capital cost estimate:
plant reclaiming rubber from tires
(200 tons of tires/day)

	Equipment	Foundations & Labor	Total
Building including offices			$ 30,000
Basement, stairs, ramps, etc.			38,300
Paved area & roads 100 yd^2			9,000
N_2 piping & plumbing			8,300
Crane (allow.)			15,000
			$100,600
Particle-izer w/overhead bin	$100,000	Included	$100,000
First conveyor (chipped tires)	11,000	$ 1,800	12,800
Chip bin	3,900	600	4,500
Chip feeder	1,600	300	1,900
Liquid N_2 tunnel	150,000	17,000	167,000
Entry duct to hammer mill no. 1	1,400	400	1,800
Hammer mill no. 1	25,700	5,400	31,100
Two-deck screen	12,800	1,900	14,700
Conveyor (rubber)	2,200	400	2,600
Conveyor (fiber & wire)	14,600	2,600	17,200
Conveyor (recycle)	2,200	400	2,600
Elevator to hammer mill no. 2	5,200	900	6,100
Single-deck screen	3,500	700	4,200
Conveyor (tramp)	9,100	1,800	10,900
Conveyor (recycle return)	3,000	600	3,600
Elevator (recycle return)	4,800	800	5,600
Elevator (rubber)	7,000	1,200	8,200
Magnetic separator (wire)	4,000	700	4,700
Magnetic separator (fine metal)	2,600	600	3,200
Bins (rubber & fine metal)	8,300	1,200	9,500
Fiber collector (pneumatic)	12,000	2,000	14,000
Insulation	3,500	Included	3,500
Power wiring	23,500	24,000	47,500
Hammer mill no. 2	17,000	3,600	20,600
			$497,800
Contractor's indirect charges			$ 50,800
Engineering & drafting			48,400
Start-up			15,000
Spare parts 5% equipment			21,400
			$734,000
Contingency 20%			147,000
Grand total			$881,000

Table 2. Manufactured cost

Calculation assumes:

Free tires	
Liquid nitrogen	\$0.037
Average production rate (i.e., 200 tons per 24 plant hours)	8-1/3 tons/hr

Weekly hours	Tons rubber/year	Manufactured cost
7 days × 24 hours	46,600	\$0.0495
5 days × 16 hours	22,064	\$0.0522
5 days × 8 hours	11,032	\$0.0559

Table 3. Variation in manufacturing costs

Variation in cost due to changes in:

1. Tire cost per ton
   - a) Tires at 25¢ each or \$25 per ton.
   - b) Tires at no cost.
   - c) Tires received with 25¢ per tire payment for disposal.
2. Liquid N_2 cost

   3.7¢/lb.
3. Level of production
   - a) 100% - 46,620 tons of rubber
     Plant works 24 hours, 7 days per week.
   - b) 47.4% - 22,064 tons of rubber
     Plant works 16 hours, 5 days per week.
   - c) 23.7% - 11,032 tons of rubber
     Plant works 8 hours, 5 days per week.

Liquid N_2 cost \$/lb	0.037	0.037	0.037
Tire cost \$/ton	25	-0-	-25
Manufacturing cost of salvage - ¢/lb of rubber produced			
Rubber 46,620 ton/yr	6.74	4.95	3.17
Rubber 22,064 ton/yr	7.01	5.22	3.44
Rubber 11,032 ton/yr	7.33	55.59	3.81

In this table, the lowest manufacturing cost indicated is $0.0317/lb of rubber. This is for a plant working 7 days per week × 24 hours per day, receiving $25.00 per ton for disposing of tires and buying liquid nitrogen at $0.037/lb.

The highest manufacturing cost indicated is $0.0733/lb of rubber. This is for a plant working 5 days per week × 8 hours per day, where the tires cost $25.00 per ton and the liquid nitrogen costs $0.037 per lb.

ECONOMY IN CRYOGENIC TIRE RECYCLING

A permanent cryogenic rubber- (and other solid waste materials) recycling plant including a prefabricated metal building would cost approximately $881,000. Operating 24 hours per day, such a plant would be capable of processing 10 tons/hour (1,000 tires/hour) of any size tire, truck or automobile. The rubber would be 98 percent clean and ready for immediate use or for further processing.

The annual cost of operating such a facility would be $1,269,100 and the net profit (after taxes) $217,000 based on 200 tons of tires per day, free tires, and a liquid nitrogen cost of $0.037/lb ($0.27/100 ft^3).

ACKNOWLEDGMENT

The cost study used in this report was prepared by W. B. Laird, Assistant Director, Airco Research Lab, Murray Hill, New Jersey.